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Polymerizable UV absorbers for the UV stabilization of polyesters. I. Design, synthesis and polymerization of a library of UV absorbing monomers

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Dedicated to Professor Phil Hodge for his outstanding lifetime achievements in organic and polymer chemistry

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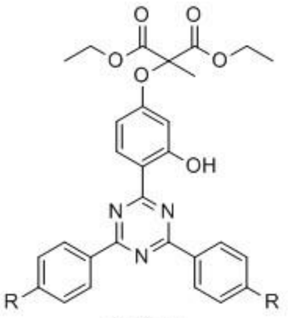
Abstract

UV stabilizers, such as Tinuvin 1577, are organic additives that are used in the polymer industry to suppress polymer photodegradation, however leaching of the stabilizers from polymers is a significant practical issue which limits the effectiveness of the stabilizers and restricts polymer lifetimes. Novel, polymerizable UV stabilizers were synthesised and copolymerized with *bis*(2-hydroxyethyl) isophthalate to yield poly(ethylene isophthalate) copolymers where the UV stabilizers are bound covalently into the polymer chains. This strategy prevents leaching of stabilizers from polymers over time, and is expected to lead to enhanced UV protection of polymers compared to the admixing of polymers with UV stabilizers of low molar mass.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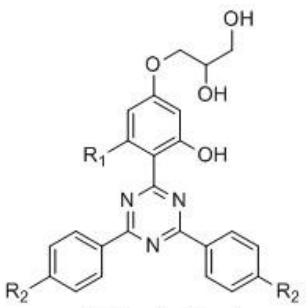
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13 R_1 = H, R_2 = OCH_3
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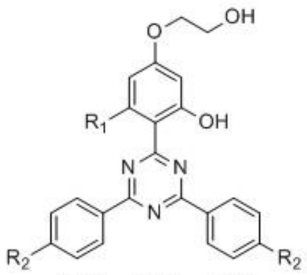
15 R_1 = OH, R_2 = H
16 R_1 = H, R_2 = Ar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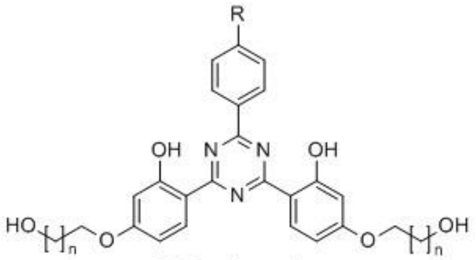
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25 R = H, n = 8
26 R = OCH_3, n = 1

Keywords: Ultraviolet**,** Degradation, Poly(ethylene terephthalate), Poly(ethylene isophthalate), UV absorber, Tinuvin 1577

Introduction

Poly(ethylene terephthalate) (PET) absorbs strongly in the ultraviolet (UV) region of the EM spectrum (Figure 1), and this can lead to photodegradation of the polymer chains and loss of polymer properties. UV stabilizer additives are normally employed to suppress the UV-induced photodegradation of polyester films, especially for those applications where the levels of UV exposure to the polymer film are high, *e.g.*, photovoltaic cells.[1] One limitation concerning the use of UV stabilizers is the loss of additive from the polymers over time by leaching, since UV stabilizers are normally low molar mass organic compounds that can be washed out through weathering actions, and this reduces their effectiveness. One way in which this leaching problem can potentially be circumvented is to lock the UV stabilizers into the polymer chains through covalent bonds.[2]

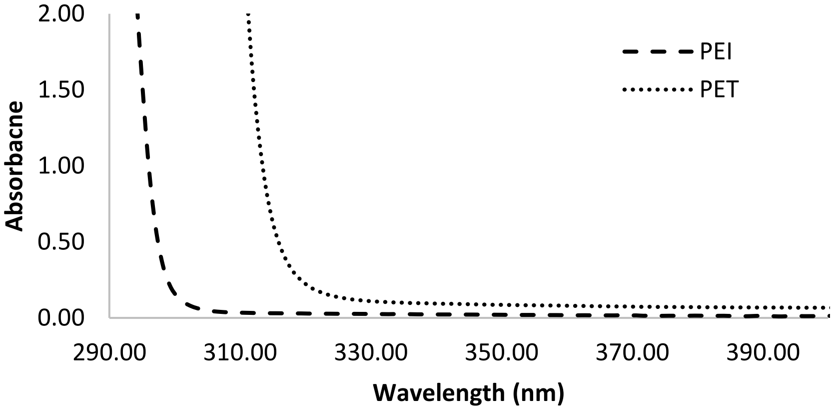

Figure 1. UV absorbance spectra of poly(ethylene isophthalate) (PEI) and poly(ethylene terephthalate) (PET).

UV degradation of PET

The photochemistry of polyester degradation is a complex area and has been studied extensively over the past fifty years. In the early 1970s, Day and Wiles[3–6] proposed mechanisms (Figure 2) to explain the formation of the three main products (-COOH , CO and CO_2) arising from the exposure of PET to oxidative and non-oxidative conditions. It was found that wavelengths below 310 nm were critical for main-chain scission and that wavelengths above 315 nm led to the production of COOH end groups. Day and Wiles postulated that carboxylic acid end groups were formed by a Norrish Type II photo-elimination reaction, involving an intramolecular rearrangement of the ester group into an olefin and carboxylic acid. CO build up was explained by a photolytic chain-scission, *via* a Norrish Type I reaction. The rate of CO_2 formation increased greatly for irradiations conducted in the presence of air, so it was evident that oxygen played a role in the mechanism. Furthermore, the hydroxyl radicals formed could give rise to fluorescent mono-/di-hydroxyl terephthalate species.

Fechine[7–9] proposed an alternative mechanism, involving a Norrish Type I reaction which proceeded through a radical pathway in the presence of oxygen, and Rivaton *et al.*[10] reported further oxidation of aldehyde to produce additional carboxylic acid end groups.

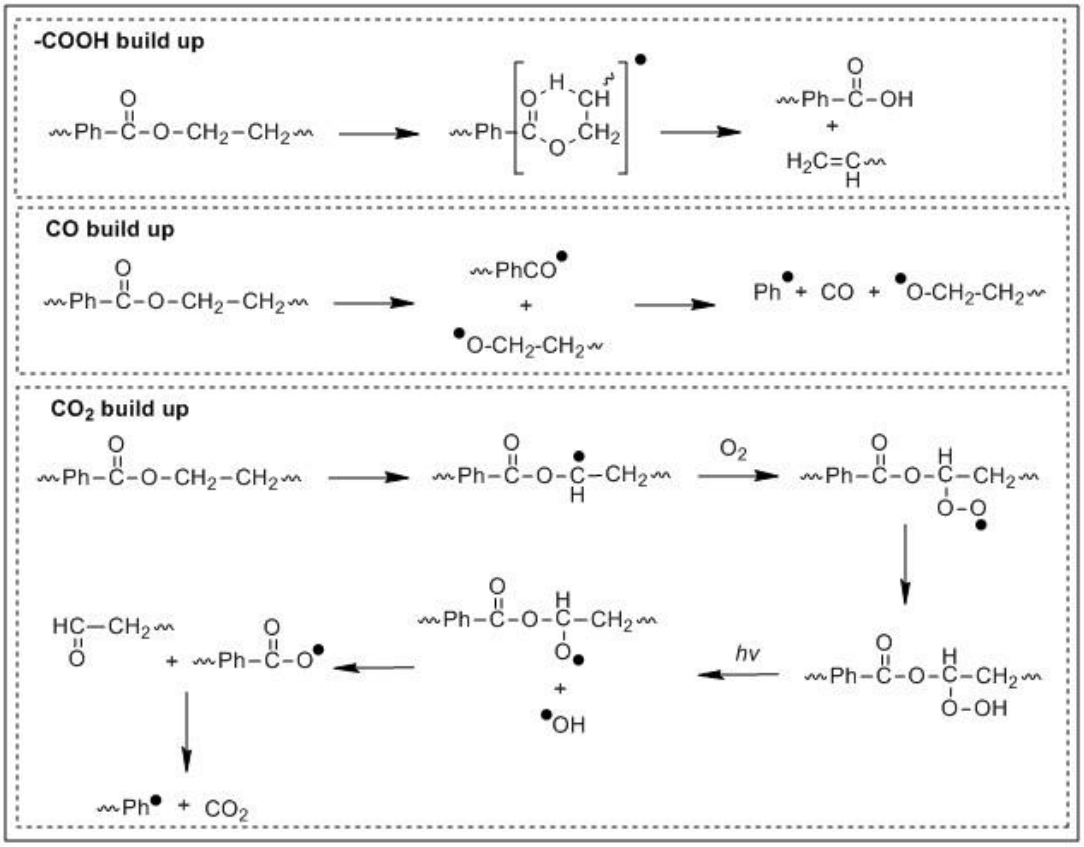

Figure 2. Mechanisms proposed by Day and Wiles for the formation of –COOH, CO and CO_2 during the photodegradation of PET.[5]

Ultraviolet absorbers

Ultraviolet absorbers (UVAs) are commercially-available polymer additives that are employed commonly in the polymer industry due to their effectiveness in protecting polymeric materials from UV radiation. They absorb UV light and dissipate the UV energy into harmless heat energy whilst remaining chemically unchanged through a process called excited state intramolecular proton transfer (ESIPT).[11–13] ESIPT is observed with planar 5- and 6-membered rings that have intramolecular hydrogen bonding (IMHB) between a phenolic hydrogen and a heteroatom. The heteroatom is normally either a nitrogen atom, from 2-(hydroxyphenyl) benzotriazole[14,15] (BT) or 2-(2-hydroxyphenyl)-1,3,5-tiazine (TA) derivatives,[2] or an oxygen atom from 2-hydroxybenzophenone (BP) or salicylate derivatives.[16]

Tinuvin 1577 (Figure 3) is one of the most effective UV stabilizers available and is the leading UVA on the market today.[17,18] This TA derivative is manufactured by BASF and is currently the UVA of choice for DuPont Teijin Films (DTF) as an additive to PET. As well as being a powerful UV screen, Tinuvin 1577 exhibits a robust IMHB, it is resilient to polar environments and it has a low yellowing index.[7,9,17,18]

One major limitation concerning the use of Tinuvin 1577, and essentially all other UVAs, is potential leaching of the stabiliser from the polymer whilst the polymer is in use. The loss of additive over time leads to an increase in the rate of UV-induced degradation and deterioration of key polymer properties, and this is of particular concern for applications where polymers are exposed to high levels of UV radiation. One way in which this can be prevented is by developing and exploiting polymerizable UVAs, where the UVA motif is an integral part of the polymer structure.

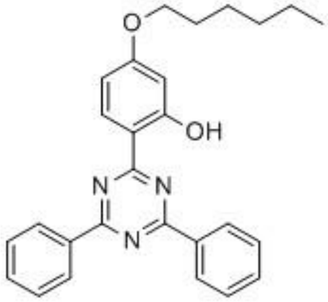

Figure 3. Tinuvin 1577.

There has been extensive work on the preparation of polymerizable UVAs bearing vinyl functionality, especially BP and BT derivatives, where the vinyl functionality allows incorporation of the UVAs into vinyl polymers through free radical polymerization routes.[19–24] Kramer *et al*. described the synthesis of TAs with vinyl moieties and the free radical copolymerization of the same with styrene and methyl methacrylate.[2,25] Recent work by Bojinov and co-workers[26–33] involved the synthesis of various polymerizable UV stabilizers with a variety of functionalities. Several of Bojinov's compounds contained both a UVA moiety and a photo-antioxidant fragment.

Compared to chain-growth polymerization, there are many fewer examples of UVAs copolymerized *via* step-growth polymerization processes. Bailey and Vogl[23,24] copolymerized BPs to yield polyamide copolymers and Kulia *et al*. copolymerized BTs with phenolic moieties in a step-growth polymerization to yield polysulfone and polycarbonate copolymers.[15] In addition to preventing leaching, Bailey and Vogl reported that polymerized UVAs reduce volatilization of the stabilizing component and that the spectral profiles of the UVAs remained unchanged upon incorporation into the polymers. The focus of the present work was on the production of polymerizable UVAs with structures related to Tinuvin 1577 for the production of polyesters through step-growth polymerization routes.

Results and Discussion

The starting point for the synthetic route to UV absorbing monomers (UVAMs) **10-19** and **24-26** was cyanuric chloride (Figure 4). Cyanuric chloride is an inexpensive building block which has been used extensively in organic synthesis due to its thermally-controlled reactivity,[34] and the UVAMs targeted were diesters, diols, and monoalcohols for ease of incorporation into polyester syntheses. Grignard and Friedel-Crafts chemistries were employed successfully to build the main chromophore frameworks around the triazine core, with one or more IMHBs being installed. Grignard reagents were used to substitute aryl, biphenyl, fluoro aryl and methoxy aryl moieties onto the triazine ring. Friedel-Crafts chemistry was an effective tool to substitute the second or final chlorine for resorcinol or phloroglucinol. The polymerizable moieties were installed *via* nucleophilic substitution with an alkyl halide such as 2-bromoethanol, 9-bromo-1-nonanol, 3-chloropropane-1,2-diol and diethyl 2-bromo-2-methylmalonate. The phenolic groups in the *para* positions with respect to the triazine rings present in compounds **5**-**9**, **22** and **23** were deprotonated under basic conditions to give phenoxide anion nucleophiles which attacked the alkyl halides. The phenolic groups in the *ortho* positions with respect to the triazine rings were protected by the strong IMHBs and did not partake in nucleophilic substitution reactions.

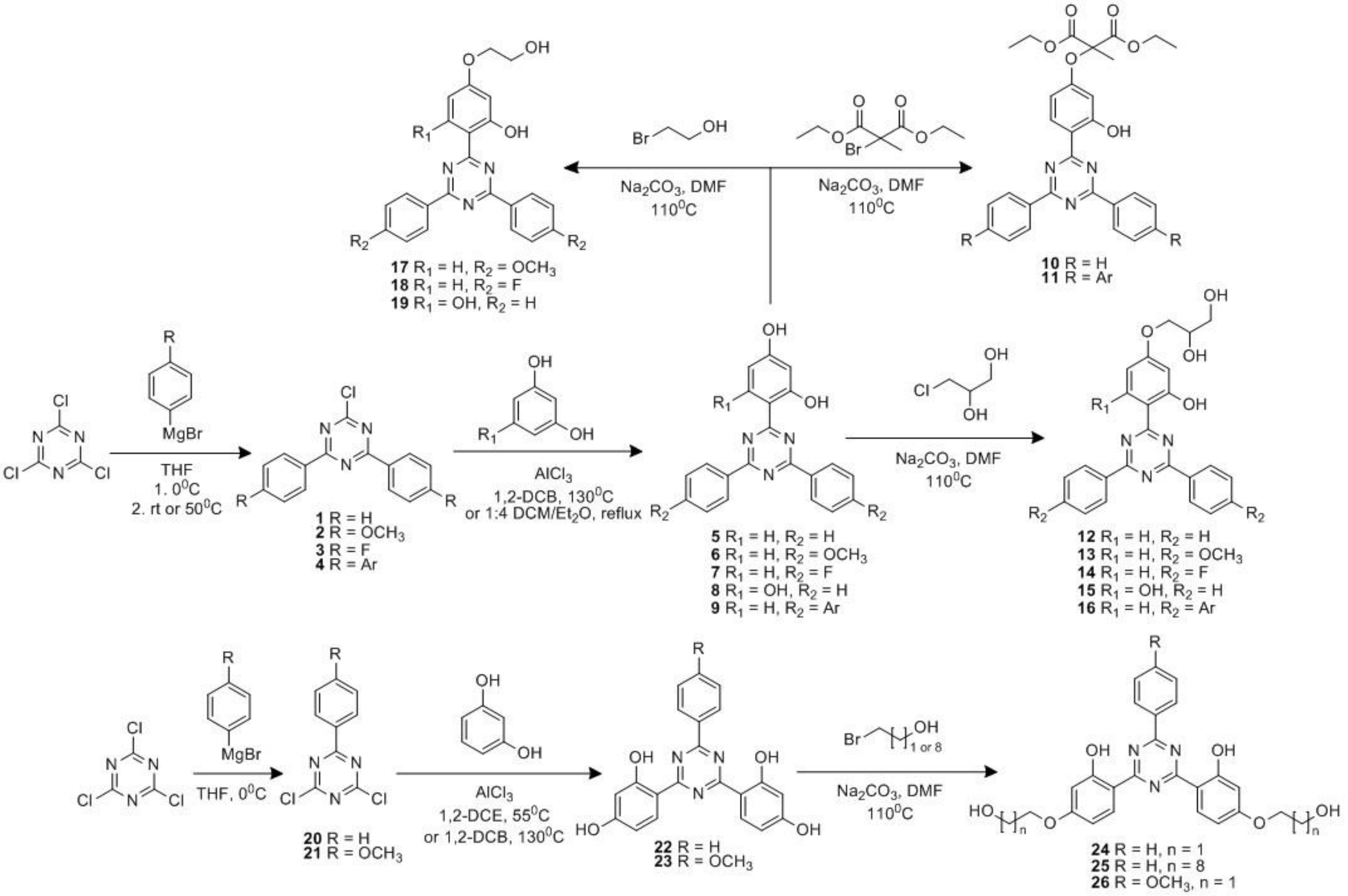

Figure 4. Synthetic routes to UVAMs **10-19** and **24-26.**

UV Analysis of UVAMs

The UV absorbance profiles of the UVAMs were compared against Tinuvin 1577 as a benchmark, and also compared against each other to understand the impact of modifying the chromophore structure on the UV absorbance profile. The UV absorbance profiles of UVAMs **10**, **12**, **14** and **18** mirrored that of Tinuvin 1577 (Figure 5). This was expected for **10** and **12** since the chromophore in these UVAMs is identical to that of the commercial UV additive. This showed that installing the polymerizable moieties on the aliphatic chain of Tinuvin 1577 was an effective way to maintain the attractive UV profile of Tinuvin 1577 whilst rending the UVAs polymerizable. The UV profiles of **14** and **18** were nearly identical despite the inductive nature of fluorine. For all of these UVAMs, the higher wavelength band is ascribed to a π-π* intramolecular charge transfer transition, and the lower wavelength band is attributed to localized π-π* transitions.

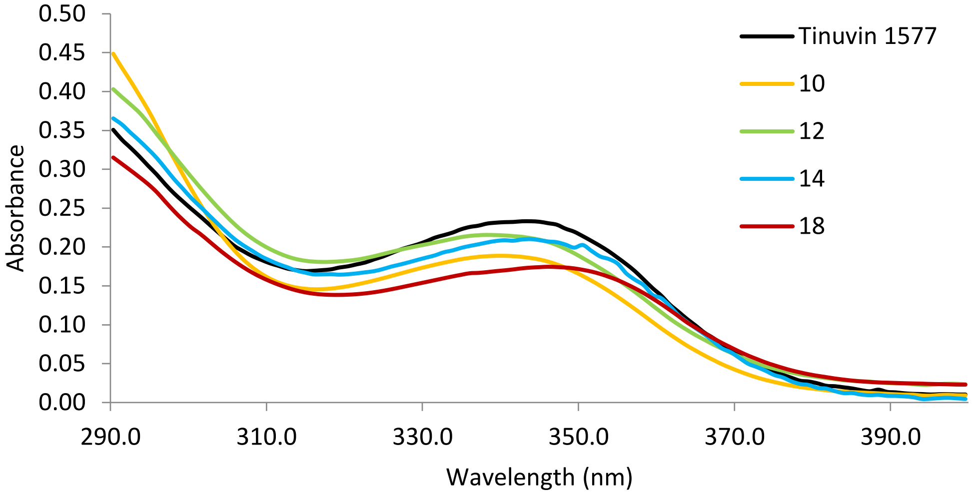

Figure 5. UV absorbance spectra of 0.1 mM solutions of UVAMs **10** (DMSO), **12** (DMSO), **14** (DMSO), **18** (DMSO) and Tinuvin 1577 ($CHCl_3$).

Increasing the conjugation and the number of *π* bonds reduced the energy gap required for electron promotion. A red-shift is commonly observed since reducing the energy needed for excitation increases the wavelength of light. The most conjugated UVAMs, **11** and **16**, were the most powerful UV absorbers in this study (Figure 6). The biphenyl groups caused a red-shift in the π-π* band which overlapped with the π-π* charge transfer transition. It is important to note that a red-shift into the visible region is undesirable as it produces a brown coloured polymeric product upon copolymerization.

The effect of an electron-donating methoxy group and an electron-withdrawing fluorine group were investigated by comparing the UV absorbance curves of **13** and **14** with Tinuvin 1577 (Figure 7). When comparing the UV spectra of **13** and Tinuvin 1577, the electron-donating methoxy groups caused a red-shift in the π-π* transitions and increased the molar absorptivity. Keck and co-workers[2,35,36] have reported that electron-donating functional groups increase the basicity of the nitrogen triazine atoms, which in turn strengthens the IMHB and contributes to the increase in extinction coefficient. The inductive effect of the fluorine atoms had little influence on the UV profile of **14**. In contrast to the methoxy functional groups, the fluorine atoms may marginally weaken the strength of the IMHB. An IMHB that is too weak is susceptible to disruption in polar environments, however the Keck group postulated that an IMHB which is too powerful is unfavorable and can hinder the radiationless deactivation by impeding the twisting vibration between the aryl and heterocyclic moieties. It is therefore important to recognize the potential of decreasing the strength of the IMHB, especially if this is achievable without damaging the UV absorbance of the UVAM.

Comparing the UV curve of **15** to Tinuvin 1577 illustrates the increase in absorbance that is observed when an additional IMHB is introduced. An additional IMHB on the same aryl ring caused a blue-shift and an increase in the molar extinction coefficient of the π-π* charge transfer transition. Keck[2,35,36] postulated that this transition relies heavily on the planarity of the orientation and an additional IMHB further reinforces this conformation to give an increase in the molar absorptivity. However, having two IMHBs on the same aryl ring raises questions as to what effect this will have on the ESIPT and radiationless deactivation process. If an IMHB is too strong then this inhibits the twisting vibration and radiationless deactivation, therefore it would be fair to assume that the twisting vibration would be inhibited to a greater extent by an additional IMHB. Furthermore, Shizuka[36] postulated that the excited molecule undergoes *cis-trans* isomerization post intramolecular proton transfer to prevent reverse intramolecular proton transfer, however one would expect the second IMHB to hinder the 180 ° rotation of the triazine-aryl bond. The situation whereby both IMHBs undergo intramolecular proton transfer is unlikely since this would disrupt the aromaticity of the molecule.

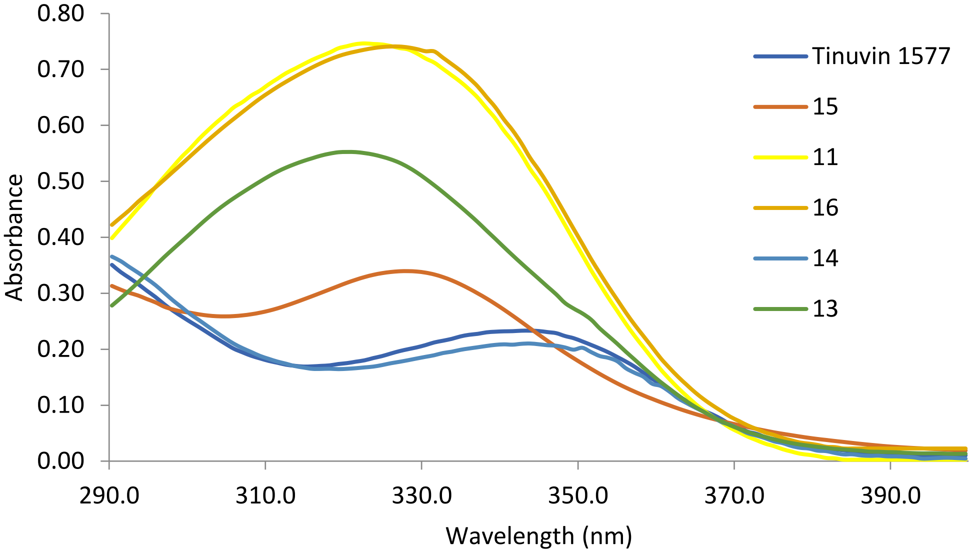

Figure 6. UV absorbance spectra of 0.1 mM solutions of Tinuvin 1577 ($CHCl_3$), **11** ($CHCl_3$), **13** (DMSO), **14** (DMSO), **15** (DMSO) and **16** (DMSO).

UVAMs **24**, **25** and **26** had higher molar extinction coefficients than Tinuvin 1577 across the 290-400 nm region (Figure 7). Increasing the number of resorcinyl moieties and the number of IMHBs caused a red-shift in both the π-π* and charge transfer transitions. A slight red-shift was observed for **25** with long hydroxyalkyl chains in comparison to the UV curve of **24** which had shorter polymerizable arms. UVAM **26** had a higher molar absorptivity between 310-350 nm than **24** and **25**, with the methoxy group causing a blue-shift in the charge transfer transition and a red-shift in the π-π* transition resulting in an overlap. Dobashi[37,38] discovered a clear relationship between the photostabilizing effect and the maximum wavelength of absorption (λ_{max}) of the UVA. Dobashi demonstrated that BP and BT ultraviolet absorbers with higher λ_{max} were the superior photostabilizers. If the same is true for TA derivatives and absorbance at longer wavelengths enhances the photostabilizing effect, then this further highlights the application potential of **24**, **25** and **26**. Furthermore, these UVAMs ought to be more adept at preventing the formation of fluorescent by-products during PET degradation, by-products which are formed by deeply penetrating low energy, high wavelength UV light.[7,9]

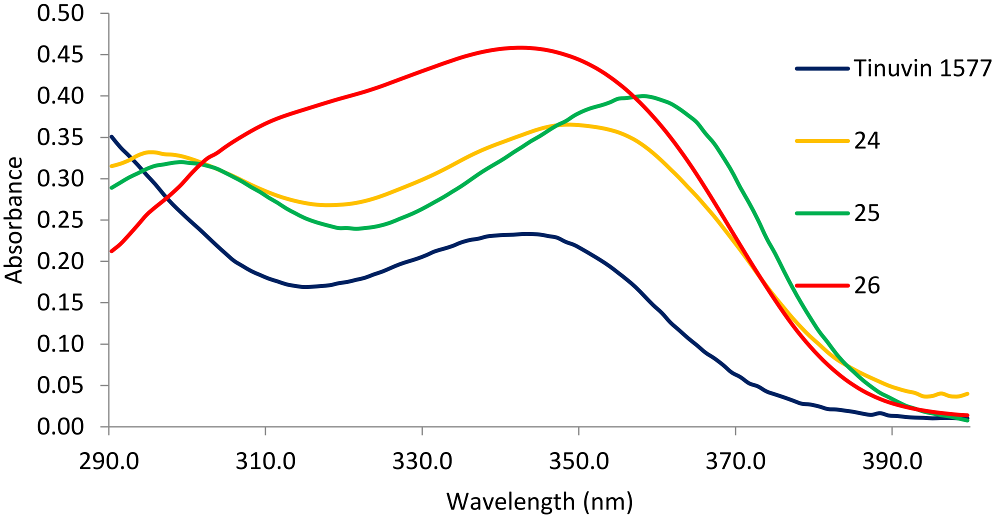

Figure 7. UV absorbance spectra of 0.1 mM solutions of Tinuvin 1577 ($CHCl_3$), **24** (DMSO), **25** (DMSO) and **26** ($CHCl_3$).

Thermal analysis of UVAMs

PET and PEI are typically synthesized at 285 °C in industry, thus the thermal stability of UVAMs is a critical characteristic to ensure that there is minimal loss of active ingredient residing in the polymer and high levels of UV protection. As a useful measure of thermal stability, the onset temperature and weight loss at 300 °C of the UVAMs were compared to Tinuvin 1577 as a benchmark. Thermogravimetric analysis (TGA) of the UVAMs was carried out in air, with the temperature being increased at a rate of 10 °C/min. The onset of degradation was calculated by differentiating the percentage weight loss curve.

UVAMs containing propanediol or glycol polymerizable moieties (**12**-**19**) showed onset temperature well above 285 ˚C, however **17** was the only UVAM from this group to display thermal stability superior to Tinuvin 1577 (Table 1). Since the precursors to UVAMs **12**-**19** were generally more thermally stable than the UVAMs themselves (data not shown), the loss of weight up to 300 ˚C could be attributed to the thermal degradation of the polymerizable fragments. This would favour introducing the UVAMs at the beginning of polymerizations and then raising the temperature of a copolymerization gradually, allowing the UVAMs to become incorporated into the polymer chains before degradation can ensue. UVAM **18** exhibited a weight loss of 2.9% at 120 °C, which was accredited to residual solvent, and this contributed to the 8.6% weight loss after 300 °C.

Increasing the number of resorcinol moieties and IMHBs increased the thermal stability of the UVAMs. UVAMs **24** and **25** contained two resorcinol moieties and displayed thermal stability superior to Tinuvin 1577, whereas **26** had properties similar to the commercial additive. UVAM **25** displayed no weight loss after 300 ˚C, which may be due to the increased stability of long chain polymerizable functional groups.

Table 1. Thermogravimetric analysis of UVAMs and Tinuvin 1577

UVA/UVAM	Weight loss at 300 ˚C (%)	Onset temperature (°C)
Tinuvin 1577	2.0	340
10	0.8	342
11	1.3	326
12	2.3	312
13	3.6	329
14	3.3	346
15	4.1	319
16	5.7	310
17	1.7	339
18	8.6	309
19	5.6	314
24	1.7	388
25	0	411
26	1.4	331

PEI-UVAM Copolymers

The polyesters prepared during this study were synthesized in a polycondensation rig using *bis*(2-hydroxyethyl) isophthalate) (BHEI) as the main monomer (Figure 8). UVAMs **10-19** and **24-26** can be incorporated into the monomer feed as comonomers since they have complementary functional groups. BHEI was selected in preference to *bis*(2-hydroxyethyl) terephthalate) (BHET) as monomer, since the product (PEI) is readily soluble in organic solvents which facilitates both polymer purification and analysis by solution state nuclear magnetic resonance (NMR) and UV spectroscopy, however the synthetic strategy is expected to be generic and can be applied to PET production and the production of other polyesters as well.

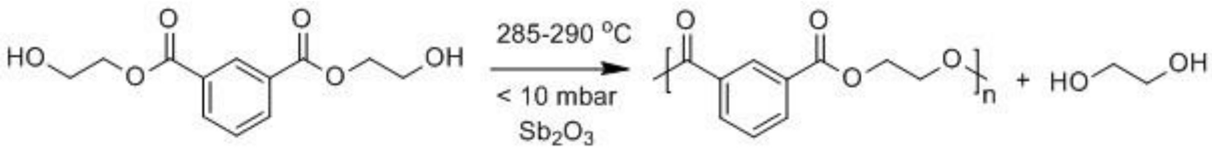

Figure 8. Step-growth polymerization of BHEI to give PEI and ethylene glycol as a by-product.

The trans-esterification reaction generated ethylene glycol which was removed by vacuum to drive the polymerizations to completion. The levels of UVAM used in the monomer feeds to confer UV protection onto the products were typically 1 wt.%. Unlike PET syntheses in the polycondensation rig wherein the stirrer revolution rate drops by 30-40 rpm due to the crystallisation of the PET chains, a significant drop in stirrer rate was not observed during the synthesis of the fully amorphous PEI. Therefore, PEI products were cast after stirring polymerizations at temperatures between 285-290 °C *in vacuo* (< 10 mbar) for 30 minutes.

The presence of polymerized UVAM residues in the PEI copolymers was confirmed by ^{1}H NMR spectroscopic analysis of the purified copolymers. Furthermore, the level of incorporation of the UVAMs into the copolymers could be calculated by integrating the phenolic resorcinyl protons in the UVAM against the aromatic protons derived from BHEI on the polymer backbone (Table 2).

There were several circumstances whereby the signals which undergo a change in chemical shift were masked under the PEI signals. Nonetheless, for the copolymerizations involving UVAMs with polymerizable alcohol moieties on short aliphatic chains a change in chemical shift was observed for the phenolic resorcinyl protons. This change was not observed for **P1** and **P11** whereby the polymerizable moieties were too far from the phenolic resorcinyl protons to induce a change in the chemical shift.

Table 2 Theoretical and calculated values for wt% and mol% of UVAMs in copolymers, Tg and molecular weight values of copolymers **P1**-**P12** and PEI

Copolymer	UVAM Mass (g)	BHEI Mass (g)	UVAM in feed		UVAM in copolymer		Tg (˚C)	$\overline{M_w}$	Đ
			wt %	mol %	wt %	mol %			
PEI	0	100	0	0	0	0	68.9	55,200	2.5
P1 Poly(EI-*co*-**10**)	0.40	39.61	1.00	0.50	0.90	0.34	66.3	43,100	2.5
P2 Poly(EI-*co*-**12**)	0.40	39.60	1.00	0.62	0.91	0.42	67.1	38,500	2.7
P3 Poly(EI-*co*-**13**)	0.40	39.70	1.00	0.54	0.89	0.36	65.8	55,000	3.9
P4 Poly(EI-*co*-**14**)	0.40	39.60	1.00	0.57	1.31	0.56	66.6	51,000	4.3
P5 Poly(EI-*co*-**15**)	0.40	40.10	1.00	0.60	0.80	0.36	67.5	54,200	3.4
P6 Poly(EI-*co*-**16**)	0.40	39.70	1.00	0.45	0.94	0.32	66.8	33,300	2.7
P7 Poly(EI-*co*-**17**)	0.40	39.50	1.00	0.56	0.97	0.41	66.1	44,900	3.5
P8 Poly(EI-*co*-**18**)	0.40	39.50	1.00	0.61	0.88	0.40	66.1	21,000	2.6
P9 Poly(EI-*co*-**19**)	0.70	69.30	1.00	0.65	0.73	0.34	65.1	23,700	3.0
P10 Poly(EI-*co*-**24**)	0.50	49.50	1.00	0.57	0.67	0.28	68.3	107,000	3.8
P11 Poly(EI-*co*-**25**)	0.93	95.00	0.97	0.38	0.51	0.15	57.6	45,700	2.9
P12 Poly(EI-*co*-**26**)	0.40	39.60	1.00	0.52	0.51	0.20	69.2	67,000	3.7

Differential scanning calorimetry (DSC) analysis of the copolymers revealed marginally lower glass transition temperatures (Tg) for the products compared to that of PEI homopolymer, with the exception of **P12** where there was a slight increase in Tg (Table 2). This is unsurprising given the low levels of UVAMs used in the copolymerizations. A melting transition was not observed for the copolymers since PEI is amorphous.

The copolymers exhibiting the lowest weight average molecular weights were **P8** and **P9** which contained monofunctional UVAMs which act as chain stoppers (Table 2). The copolymerization of the monofunctional **17** did yield a copolymer with a high $\overline{M_w}$ of 44,900, however the bifunctional derivative of **17**, UVAM **13**, was copolymerized at similar levels and generated a copolymer with a higher $\overline{M_w}$ still (55,000).

UV Analysis of UVAM-Containing Copolymers

UVAMs with the same chromophore as Tinuvin 1577 were copolymerized with BHEI to give **P1** and **P2**, and the copolymers exhibited similar UV profiles with λ_{max} in the region of 340-343 nm (Figure 9). The UV spectra showed no protrusion into the visible region, however absorbance levels between 370-400 nm were very weak. Work carried out by Fechine[9] demonstrated that UV light above 340 nm was responsible for the formation of fluorescent mono-hydroxyl species. Therefore, UVAMs **10** and **12** would be less effective in preventing the formation of fluorescent products from photodegradation at long wavelengths.

UVAMs **13**, **15** and **16** had chromophores different to that of Tinuvin 1577, and the copolymers **P3**, **P5** and **P6** displayed superior molar absorptivity at wavelengths 290-400 nm in comparison to **P1** and **P2**. Despite the fluorinated aryl rings, **14** mimicked the UV profile of Tinuvin 1577, and for that reason the copolymer **P4** had an identical UV profile to that of **P1** and **P2**. The copolymer with the highest molar absorptivity was **P3**, which contained 0.36 mol % of polymerized UVAM **13**, surprisingly outperforming **P6** which contained 0.30 mol % of the more potent UVAM **16**. Wavelengths between 310-315 nm are critical for polymer degradation, leading to the production of COOH end groups in the bulk and front and rear surfaces of polymer films.[4,39] Therefore UVAMs **13** and **16** possess great potential for combating UV degradation, specifically chain scissions and the formation of acid end groups. No significant red- or blue-shifts were observed when comparing the λ_{max} of **P3**-**P6** to that of the free monomers. UVAM **15** contained two IMHBs and the UV spectrum of **P5** showed an increased absorbance at wavelengths above 365 nm in comparison to **P3**, **P4** and **P6**. This shows that **15** is more adept at protecting the polymer from the formation of fluorescent mono-/di-hydroxyterephthalate by-products caused by deeply penetrating low energy UV light.

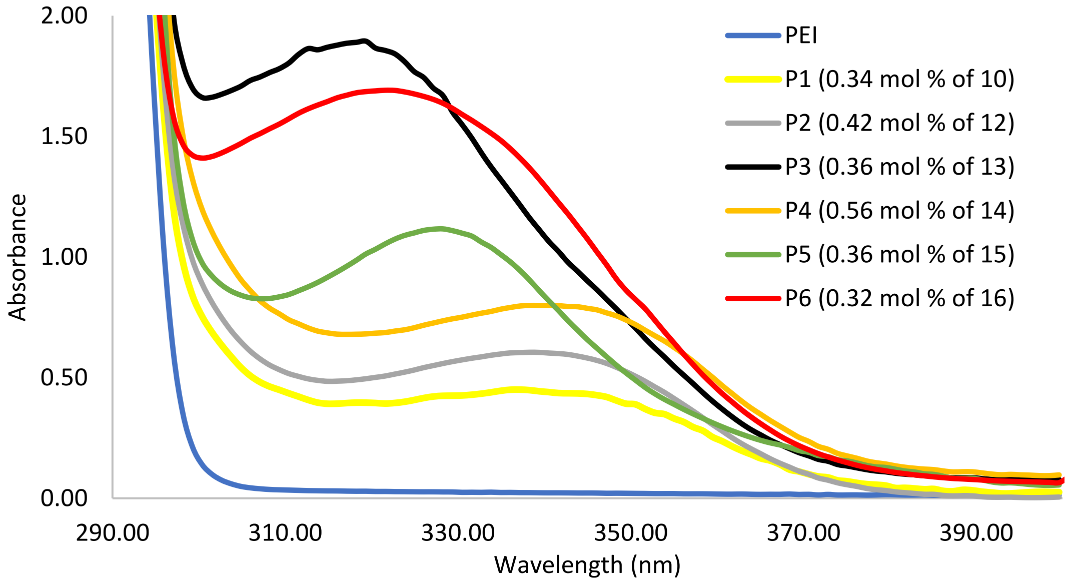

Figure 9. UV absorption spectra of 10 mg/mL solutions of copolymers **P1**-**P6** and PEI in $CHCl_3$.

At 1 wt % loadings of UVAM **24** and **25** in the monomer feed, the former showed a considerably stronger molar absorptivity after copolymerization and a 10 nm blue-shift of the λ_{max} was observed upon copolymerization of UVAM **25** (Figure 10). UVAM **26** had a higher molar absorptivity in comparison to the less conjugated **24** and **25**, which resulted in copolymer **P12** exhibiting a higher molar extinction coefficient in comparison to **P10** and **P11**. Taking into consideration all the PEI copolymers in this study, **P5**, **P10**, **P11** and **P12** showed the strongest coverage at wavelengths above 355 nm. The copolymers reported in Figure 10 contained UVAMs with two IMHBs which enhanced coverage at longer UV wavelengths, and **24** was identified as the UVAM which provided the highest molar absorptivity at longer wavelengths. Therefore **15**, **24**, **25** and **26** seem to be the most efficient UVAMs for preventing the formation of fluorescent materials during photodegradation.

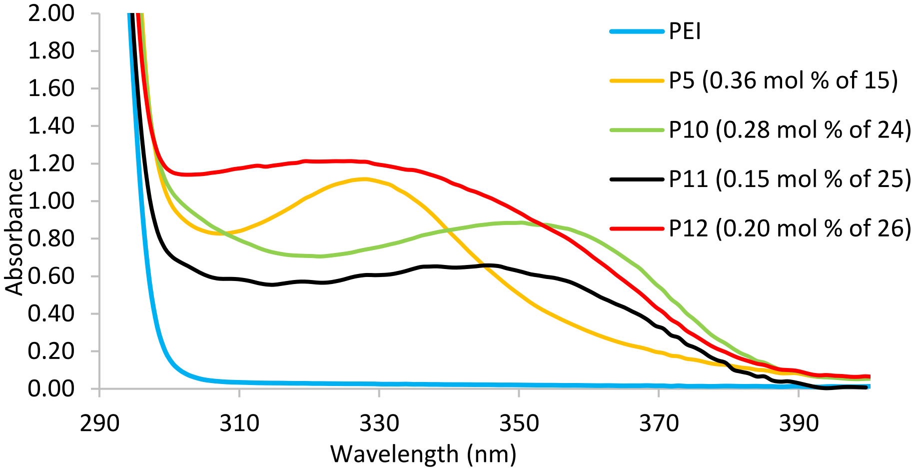

Figure 10. UV absorbance spectra of 10 mg/mL solutions of copolymers **P5**, **P10**, **P11**, **P12** and PEI in $CHCl_3$.

The UV absorbance spectra of copolymers containing bifunctional UVAMs displayed higher molar extinction coefficients than the copolymers containing their monofunctional counterparts (Figure 11). Bifunctional **15** showed increased UV absorbance compared to the monofunctional **19**, even although the level of incorporation measured by ^{1}H NMR for both monomers was similar. When comparing **P4** and **P8**, there was a significant difference in the intensity of the UV curves and the level of incorporation as judged from the ^{1}H NMR spectra, with the bifunctional UVAM **14** showing much higher levels of incorporation than the monofunctional UVAM **18**. One thing to consider for UVAMs **12**-**16** is that the reactivity of the polymerizable hydroxyl groups of the propanediol moiety are not identical, with one being a primary alcohol and the other a secondary alcohol. It can be predicted that even higher levels of incorporation and higher molar absorptivity could be gained from using bifunctional UVAMs bearing two primary alcohol functional groups.

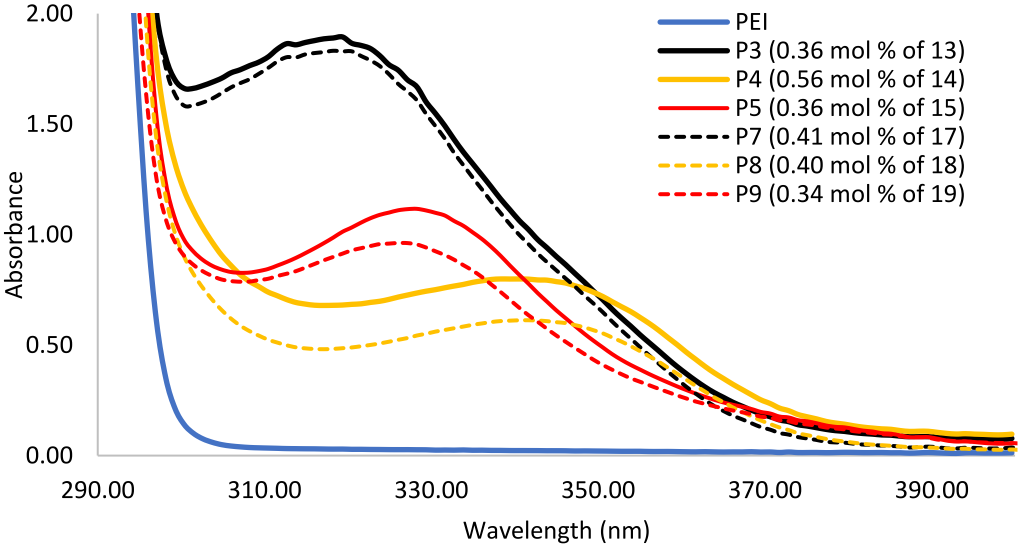

Figure 11. UV absorption spectra of 10 mg/mL solutions of copolymers **P3**, **P4**, **P5**, **P7**, **P8**, **P9** and PEI in $CHCl_3$.

At 1 wt % loadings of UVAM **24** and **25** in the monomer feed, the former showed a considerably higher molar absorptivity after copolymerization and a 10 nm blue-shift of the λ_{max} was observed upon copolymerization of UVAM **25** (Figure 10). UVAM **26** had a higher molar absorptivity in comparison to the less conjugated **24** and **25**, which resulted in copolymer **P12** exhibiting a higher molar extinction coefficient in comparison to **P10** and **P11**. Taking into consideration all the PEI copolymers in this study, **P5**, **P10**, **P11** and **P12** showed the strongest coverage at wavelengths above 355 nm. The copolymers reported in Figure 10 contained UVAMs with two IMHBs which enhanced coverage at longer UV wavelengths, and **24** was identified as the UVAM which provided the highest molar absorptivity at longer wavelengths. Therefore **15**, **24**, **25** and **26** are expected to be the most efficient UVAMs for preventing the formation of fluorescent materials during photodegradation.

Conclusions

A library of novel ultraviolet absorber monomers (UVAMs) for use in step-growth polymerizations have been synthesized using cyanuric chloride as a synthetic starting point. Grignard and Friedel-Crafts chemistries were employed to construct the core chromophore structures, with the structures of the UVAMs being based on the chromophore of the commercial UVA Tinuvin 1577. A wider and stronger UV absorbance was generally observed when increasing the number of IMHBs, electron density and conjugation of the chromophores. The UVAMs exhibited more than satisfactory thermal stability for polyester synthesis *via* step-growth polymerization and for polyester processing, and it ought not to be over-looked that these novel UVAMs are potentially interesting low molar mass UV stabilizers in their own right.

UVAMs were incorporated successfully into PEI through copolymerization. ^{1}H NMR and UV spectroscopic analysis of the copolymers showed incorporation of the UVAMs, with only low levels of UVAM being required to change dramatically the UV absorption profiles of the copolymers. The majority of copolymerized UVAMs displayed no blue- or red-shifts, which indicated that the UV profiles of most of the monomers were unaffected by copolymerization and that the IMHBs were present and correct in the copolymers. Overall, a new family of UVAMs has been set in place, and the polyesters derived from these UVAMs are expected to have enhanced resistance to UV degradation compared to the parent polymers.

Experimental Section

General. BHEI was provided by DuPont Teijin Films (DTF). All other chemicals used were of analytical reagent grade and were commercially available from Aldrich, Fisher or VWR. All solvents used in this study did not require further purification. Anhydrous THF, diethyl ether, hexane and DCM were obtained from an SPS solvent drying system. The solvents and reagents were used as received without any further purification unless indicated otherwise.

A Perkin Elmer Spectrum One Fourier Transform Infrared (FT-IR) spectrometer was used to record FT-IR spectra. The spectra were recorded using Attenuated Total Reflectance (ATR) within the range 400 to 4000 cm^{-1}. NMR spectra were recorded on Bruker DPX 400 and DRX 500 instruments in the NMR Laboratory at the University of Strathclyde, for ^{1}H, ^{13}C and ^{19}F nuclei. The chemical shifts (δ) are quoted in part per million (ppm), relative to the residual proton resonances of the solvent, and coupling constants (J values) in Hz. Multiplicities for the ^{1}H NMR spectra are abbreviated as: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. In cases where superimposition of signals arose, the signals were reported as a multiplet (m). $CDCl_3$ and d_6-DMSO were used as NMR solvents. High resolution mass spectrometry (HRMS) was carried out in the Strathclyde Institute of

Pharmacy and Biomedical Sciences (SIPBS). HRMS was performed using a Thermo Scientific-Exactive Orbitrap Mass Spectrometer. Methanol was used as the solvent and the scan range was 75-1200 *m/z*. Gas chromatography mass spectrometry (GC-MS) was carried out using an Agilent Technologies 7890A GCMS with a RESTEK RXi-5Sil MS column. Samples were dissolved in $CHCl_3$ and helium was used as the gas carrier at a flow rate of 1 mL/min. The ions were produced by electron ionization (EI) using a nitrogen laser at 337 nm. UV-Visible absorption spectra were acquired using a Photonics CCD array UV-Vis spectrophotometer with a 1 mm pathlength quartz cell. DMSO and $CHCl_3$ were used as solvents and the scan range was 290-500 nm. Thermogravimetric analysis of UVAMs was performed using a Perkin Elmer TGA 7. Approximately 10 mg of sample was heated in air at a rate of 10 °C/min. from 40 °C to 500 °C. Uncorrected melting points were determined in capillary tubes using a Gallenkamp Griffin Melting Point Apparatus. DSC analysis of polymer samples was carried out at DTF using a 6000 Enhanced Single-Furnace DSC. The samples were heated from -20 °C to 310 ° at a rate of 20 °C/min., cooled back to -20 °C at a rate of 50 °C/min. and then reheated to 310 °C at a rate of 20 °C/min. Molecular weight determination of polymers was carried out by Intertek using a Viscotek GPC Max instrument with refractive index detection. The samples were dissolved in hexafluoroisopropanol (HFIP) and passed through a PLgel HFIP Gel Column at a flow rate of 0.7 mL/min at 40 °C.

2-Chloro-4,6-diphenyl-1,3,5-triazine (1). 1 M Phenylmagnesium bromide in THF (250 mL, 0.25 mol) was added dropwise to a solution of cyanuric chloride (20.00 g, 0.11 mol) in anhydrous THF (300 mL) under nitrogen, whilst maintaining the temperature at 0 °C. Once the addition was complete, the mixture was stirred at room temperature for 16 hours and poured into cold 10% v/v aqueous HCl (200 mL). The THF was removed under reduced pressure and the organic product was extracted with $CHCl_3$ (3×150 mL). The organic layer was washed with water (2×150 mL) and brine (100 mL), dried over anhydrous sodium sulfate and the solvent removed under reduced pressure to give a purple/red coloured solid. The crude product was purified by grinding into a fine powder, suspending and washing with MeOH (3×100 mL). The product was dried at 70 °C *in vacuo* (60 mbar) to yield 19.07g (67%) of **1** as a white powder. HRMS: found *m/z* 268.0635 $(M+H)^+$; calculated *m/z* 268.0642. M. pt. expected: 139 - 140 °C;[40] found: 137 - 139 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3049, 1537, 1490. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.54-7.58 (m, 4H), 7.64 (m, 2H), 8.62-8.64 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 129.0, 129.6, 133.8, 134.6, 172.4, 173.6

2-Chloro-4,6-*bis*(4-methoxyphenyl)-1,3,5-triazine (2). 0.5 M 4-Methoxyphenylmagnesium bromide in THF (45 mL, 25.00 mmol) was added to a stirred solution of cyanuric chloride (1.84 g, 10.00 mmol) in anhydrous THF (25 mL) under nitrogen, whilst maintaining the temperature at 0 °C. Once the addition was complete, the reaction mixture was stirred at room temperature for 16 hours and poured into cold 10% v/v aqueous HCl (100 mL). The THF was removed under reduced pressure and the organic product was extracted with $CHCl_3$ (2×50 mL). The organic layer was washed with water (2×100 mL) and brine (50 mL), dried over anhydrous sodium sulfate and the solvent removed under reduced pressure. The crude solid was purified by grinding into a fine powder, suspending and washing with MeOH (3×100 mL). The white coloured product was dried at 40 °C *in vacuo* (60 mbar) to yield **2** (1.57 g, 48%). HRMS: found *m/z* 328.0848 $[M+H]^+$; calculated *m/z* 328.0847. M. pt. expected: 195-197 °C;[41] found: 194-195 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3017, 2973, 2935, 1516, 1241. ^1H NMR (500 MHz, $CDCl_3$) δ: 3.92 (s, 6H), 7.01 (d, *J* 9.0 Hz, 4H), 8.47 (d, *J* 9.0 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.5, 114.1, 127.0, 131.4, 164.1, 171.7, 172.6.

2-Chloro-4,6-*bis*(4-fluorophenyl)-1,3,5-triazine (3). 1 M 4-Fluorophenylmagnesium bromide in THF (30 mL, 0.03 mol) was added dropwise to a stirred solution of cyanuric chloride (1.84 g, 0.01 mol) in anhydrous THF (30 mL) under nitrogen, whilst maintaining the temperature at 0 °C. Once the addition was complete, the mixture was stirred for 16 hours at room temperature and then poured into cold 10% v/v aqueous HCl (50 mL). The THF was removed under reduced pressure and the organic product was extracted with $CHCl_3$ (2×50 mL). The organic layer was washed with water (2×50 mL) and brine (50 mL), dried over anhydrous sodium sulfate and the solvent removed under reduced pressure. The crude solid was purified by grinding into a fine powder, suspending and washing with MeOH (3×100 mL). The white coloured product was dried at 40 °C *in vacuo* (60 mbar) to yield **3** (1.52 g, 50%). HRMS: found *m/z* 304.0448 $[M+H]^+$; calculated *m/z* 304.0448. M. pt. expected: 177-180 °C;[42] found: 176-178 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3116, 3072, 1531, 1492. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.19-7.26 (m, 4H), 8.61-8.66 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 115.5 (d, *J* 22Hz), 129.9 (d, *J* 3 Hz), 131.3 (d, *J* 9 Hz), 166.0 (d, *J* 254 Hz), 171.6, 171.8. ^{19}F NMR (400 MHz, $CDCl_3$) δ: -104.7 (m, 2F).

2,4-*Bis*([1,1'-biphenyl]-4-yl)-6-chloro-1,3,5-triazine (4). 0.5 M 4-Biphenylmagnesium bromide in THF (50.00 mL, 25.00 mmol) was added dropwise to a stirred solution of cyanuric chloride (1.53 g, 8.33 mmol) in anhydrous THF (100 mL) under nitrogen, whilst maintaining the temperature at 0 °C. Once the addition was complete, the mixture was stirred for 16 hours at 50 °C and poured into 10% v/v aqueous HCl (100 mL). The THF was removed under reduced pressure and the organic product was extracted with $CHCl_3$ (2×50 mL). The organic layer was washed with water (2×50 mL) and brine (50 mL), and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and purified by grinding into a fine powder, suspending and washing with MeOH (3×100 mL). The white coloured powder was dried at 70 °C *in vacuo* (60 mbar) to yield **4** (2.00 g, 57%). HRMS: found *m/z* 420.1263 $[M+H]^+$; calculated *m/z* 420.1262. M. pt. found: 164-167 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3035, 3034, 1526, 1489. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.43-7.47 (m, 2H), 7.51-7.54 (m, 4H), 7.71-7.73 (m, 4H), 7.82 (d, *J* 8.5 Hz, 4H), 8.73 (d, *J* 8.5 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 126.8, 127.0, 127.8, 128.5, 129.5, 132.8, 139.5, 145.8, 171.6, 172.6.

4-(4,6-Diphenyl-1,3,5-triazin-2-yl)benzene-1,3-diol (5). $AlCl_3$ (1.91 g, 14.60 mmol) was added to a suspension of 2-chloro-4,6-diphenyl-1,3,5-triazine **1** (3.00 g, 11.20 mmol) and resorcinol (1.49 g, 13.50 mmol) in 1,2-dichlorobenzene (250 mL) and stirred at 130 °C for 16 hours under nitrogen. The mixture was cooled to room temperature and quenched with 10% v/v aqueous HCl (150 mL). After stirring at room temperature for 1 hour, the red coloured precipitate was collected by filtration, washed with water (150 mL) and dried at 70 °C *in vacuo* (60 mbar). No further purification was required and the red coloured crude product **5** (3.03 g, 78%) was used in the subsequent step. M. pt. Found: 272 °C. HRMS: found *m/z* 342.1235 $(M+H)^+$; calculated *m/z* 342.1237. UV λ_{max} (0.1 mM in DMSO): 343 nm (Ɛ = 24,000 cm^{-1} M^{-1}). FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3150-3400, 3057, 1508, 1519, 1504. ^1H NMR (500 MHz, DMSO-d_6) δ: 6.38 (d, *J* 2.0 Hz, 1H), 6.53 (dd, *J* 9.0, 2.0 Hz, 1H), 7.63-7.65 (m, 4H) 7.69-7.72 (m, 2H), 8.48 (d, *J* 9.0 Hz, 1H), 8.52-8.54 (m, 4H), 10.48 (s, 1H), 13.22 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 103.5, 109.36, 109.44, 129.0, 129.5, 132.0, 133.7, 135.2, 164.2, 164.8, 170.0, 171.1.

4-(4,6-*Bis*(4-methoxyphenyl)-1,3,5-triazin-2-yl)benzene-1,3-diol (6). $AlCl_3$ (0.12 g, 9.2 mmol) was added to a suspension of 2-chloro-4,6-*bis*(4-methoxyphenyl)-1,3,5-triazine **2** (0.25 g, 0.76 mmol) and resorcinol (0.10 g, 0.92 mmol) in 1,2-dichlorobenzene (10 mL) and the reaction mixture was stirred at 130 °C for 16 hours under nitrogen. The reaction mixture was cooled to room temperature and 10% v/v aqueous HCl (30 mL). The suspension was spun in a centrifuge at 1000 rpm for 5 min. and the supernatant was removed. The solid residue was collected by filtration, washed with water (100 mL) and dried at 70 °C *in vacuo* (60 mbar). No further purification was necessary and the red coloured crude solid **6** (0.33 g, 90%) was used in the subsequent step. HRMS: found *m/z* 400.1307 $(M-H)^-$; calculated *m/z* 400.1303. M. pt. found: 253-255 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 2800-3500, 3076, 2837, 1504, 1145. UV λ_{max} (0.1 mM in DMSO): 318 nm (Ɛ = 53,000 cm^{-1} M^{-1}). TGA (Air): Weight loss at 300 °C (2.56%); Onset temperature (333 °C). ^1H NMR (500 MHz, DMSO-d_6) δ: 3.87 (s, 6H), 6.36 (d, *J* 2.2 Hz, 1H), 6.49 (dd, *J* 8.8, 2.2 Hz, 1H), 7.13 (d, *J* 8.9 Hz, 4H), 8.42-8.45 (d, *J* 8.8 Hz, 1H), 8.44 (d, *J* 8.9 Hz, 4H) 10.42 (s, 1H), 13.40 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 56.0, 103.5, 109.1, 109.6, 114.9, 127.5, 130.9, 131.8, 163.9, 164.2, 164.5, 169.2, 170.7.

4-(4,6-*Bis*(4-fluorophenyl)-1,3,5-triazin-2-yl)benzene-1,3-diol (7). $AlCl_3$ (0.13 g, 0.99 mmol) was added to a suspension of 2-chloro-4,6-*bis*(4-fluorophenyl)-1,3,5-triazine **3** (0.25 g, 0.82 mmol) and resorcinol (0.11 g, 0.99 mmol) in 1,2-dichlorobenzene (10 mL) and the mixture was stirred at 130 °C for 3 hours under nitrogen. The reaction mixture was cooled to room temperature and 10% v/v aqueous HCl (30 mL) was added and stirred for 30 mins. The pink coloured precipitate was collected by filtration, washed with water (50 mL) and dried at 70 °C *in vacuo* (60 mbar). No further purification was required and the pink coloured solid **7** (0.26 g, 84%) was used in the subsequent step. HRMS: found *m/z* 376.0909 $[M-H]^-$; calculated *m/z* 376.0903. M. pt. found: 333-335 °C. FT-IR (ATR): $\bar{v}$/ cm^{-1}: 3250-3500, 3072, 1519, 1504, 1142. UV λ_{max} (0.1 mM in DMSO): 342 nm (Ɛ = 21,000 cm^{-1} M^{-1}). TGA (Air): Weight loss at 300 °C (4.78%); Onset temperature (325 °C). ^1H NMR (500 MHz, DMSO-d_6) δ: 6.32 (d, *J* 2.4 Hz, 1H), 6.46 (dd, *J* 8.8, 2.4 Hz, 1H), 7.39 (m, 4H), 8.37 (d, *J* 8.8 Hz, 1H), 8.48-8.50 (m, 4H), 10.45 (s, 1H), 12.99 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 103.5, 109.27, 109.32, 116.5 (d, *J* 23 Hz), 129.1 (d, *J* 3 Hz), 131.6 (d, *J* 10 Hz), 132.0, 164.2, 164.8, 165.1 (d, *J* 245 Hz), 168.9, 171.0. ^{19}F NMR (400 MHz, DMSO) δ: -106.1 (m).

2-(4,6-Diphenyl-1,3,5-triazin-2-yl)benzene-1,3,5-triol (8). Phloroglucinol (0.4664 g, 3.70 mmol) and 2-chloro-4,6-diphenyl-1,3,5-triazine **1** (0.66 g, 2.47 mmol) were added to a 1:4 mixture of anhydrous DCM and anhydrous diethyl ether (25 ml). $AlCl_3$ (0.4931 g, 3.70 mmol) catalyst was added and the mixture was refluxed for 16 hours under nitrogen. The solvent was removed under reduced pressure and the solid was suspended in 10% v/v aqueous HCl (25 mL). The suspension was transferred to a centrifuge tube and spun at 3400 rpm for 5 mins. The supernatant was removed, and the pellet was re-suspended and spun at 3400 rpm for 5 mins. in distilled water (25 mL) and the supernatant removed. The crude product was collected by filtration and dried at 70 °C *in vacuo* (60 mbar). No further purification was required and the red coloured crude product **8** (0.79 g, 60%) was used in the subsequent step. HRMS: found *m/z* 356.1046 $(M-H)^-$; calculated *m/z* 356.1041. M. pt. found: 244-245 °C. FT-IR (ATR): $\bar{v}$/ cm^{-1}: 3150-3500, 3026, 1508, 1479, 1282. UV λ_{max} (0.1 mM in DMSO): 330 nm (Ɛ = 33,000 cm^{-1} M^{-1}). TGA (Air): Weight loss at 300 °C (2.80%); Onset temperature (372 °C). ^1H NMR (400 MHz, DMSO) δ: 5.94 (s, 2H), 7.66-7.70 (m, 4H), 7.70-7.76 (m, 2H), 8.40 (d, *J* 7.3 Hz, 4H), 10.57 (s, 1H), 13.57 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ: 95.6, 95.7, 128.5, 129.3, 133.79, 133.82, 164.2, 165.0, 168.3, 170.5.

4-(4,6-Di([1,1'-biphenyl]-4-yl)-1,3,5-triazin-2-yl)benzene-1,3-diol (9). 2,4-*Bis*([1,1'-biphenyl]-4-yl)-6-chloro-1,3,5-triazine **4** (2.00 g, 4.76 mmol), resorcinol (0.63 g, 5.72 mmol) and $AlCl_3$ (0.83 g, 6.19 mmol) were added to 1,2-dichlorobenzene (100 mL) and stirred at 130 °C for 16 hours under nitrogen. The mixture was cooled to room temperature, 10% v/v aqueous HCl (200 mL) was added and the suspension was stirred at room temperature for 30 minutes. The precipitate was collected by filtration and washed with water (100 mL). The red coloured crude product **9** (1.51 g, 64%) was dried at 70 °C *in vacuo* (60 mbar); no further purification was required and **9** was used in the subsequent step. HRMS: found *m/z* 494.1862 $(M+H)^+$; calculated *m/z* 494.1863. M. pt. found: 264-266 °C. FT-IR (ATR): $\bar{v}$/ cm^{-1}: 2900-3550, 3057, 3030, 1506, 1254. UV λ_{max} (0.1 mM in DMSO): 322 nm (Ɛ = 60,000 cm^{-1} M^{-1}). TGA (Air): Weight loss at 300 °C (7.76%); Onset temperature (336 °C). ^1H NMR (400 MHz, DMSO-d_6) δ: 6.40 (d, *J* 2.3 Hz, 1H), 6.55 (dd, *J* 8.9, 2.3 Hz, 1H), 7.46 (t, *J* 7.3 Hz, 2H), 7.51-7.56 (m, 4H), 7.79 (m, 4H), 7.93 (d, *J* 8.5 Hz, 4H), 8.50 (d, *J* 8.9 Hz, 1H), 8.60 (d, *J* 8.5 Hz, 4H), 10.51 (s, 1H), 13.29 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 103.0, 108.9, 109.0, 127.0, 127.2, 128.4, 129.08, 129.11, 131.5, 133.6, 138.9, 144.6, 163.8, 164.3, 169.1, 170.

Diethyl 2-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)-3-hydroxyphenoxy)-2-methylmalonate (10). A mixture of 4-(4,6-diphenyl-1,3,5-triazin-2-yl)benzene-1,3-diol **5** (0.25 g, 0.73 mmol) and Na_2CO_3 (0.15 g, 1.46 mmol) in DMF (20 mL) was heated to 70 °C. A solution of diethyl 2-bromo-2-methylmalonate (0.20 g, 0.81 mmol) in DMF (10 mL) was added slowly, and once the addition was complete the mixture was heated at 110 °C overnight. The mixture was filtered whilst hot, the solvent was removed from the filtrate under reduced pressure and the residue was redissolved in ethyl acetate/MeOH (8/2, v/v, 50 mL). The organic layer was washed with 5% v/v aqueous acetic acid (25 mL), 0.25 M aqueous NaHCO$_3$ (25 mL) and brine (25 mL). The solvent was dried using sodium sulfate and removed under reduced pressure. The crude product was suspended in MeOH (40 mL), filtered and the off-white coloured powder was dried at 70 ˚C *in vacuo* (60 mbar) to yield **10** (0.23 g, 60.5%). HRMS: found *m/z* 514.1976 (M+H)$^+$; calculated *m/z* 514.1973. M. pt. found: 122-124 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3031, 2981, 1755, 1735, 1525, 1508, 1271, 1139. UV λ_{max} (0.1 mM in CHCl$_3$): 340 nm (Ɛ = 19,000 cm^{-1} M^{-1}). TGA (Air): Weight loss at 300 °C (0.81%); Onset temperature (342 °C). ^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.31 (t, *J* 7.1 Hz, 6H), 1.92 (s, 3H), 4.33 (q, *J* 7.1 Hz, 4H), 6.61 (d, *J* 2.5 Hz, 1H), 6.66 (dd, *J* 8.9, 2.5 Hz, 1H), 7.57-7.60 (m, 4H), 7.65 (m, 2H), 8.63-8.65 (m, 5H), 13.45 (s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 14.0, 20.8, 62.5, 82.6, 106.5, 110.6, 112.5, 128.9, 129.0, 131.2, 133.1, 135.3, 160.7, 163.7, 168.3, 170.6, 171.2.

Diethyl 2-(4-(4,6-di([1,1’-biphenyl]-4-yl)-1,3,5-triazin-2-yl)-3-hydroxyphenoxy)-2-methylmalonate (11). A solution of 4-(4,6-di([1,1’-biphenyl]-4-yl)-1,3,5-triazin-2-yl)benzene-1,3-diol **9** (0.50 g, 1.01 mmol) and Na$_2$CO$_3$ (0.22 g, 2.02 mmol) in DMF (50 mL) was stirred at 70 °C for 1 hour. A solution of diethyl 2-bromo-2-methylmalonate (0.31 g, 1.22 mmol) in DMF (50 mL) was added dropwise, and once the addition was complete the mixture was stirred at 110 °C for 16 hours. The mixture was filtered whilst hot and the solvent was removed under reduced pressure. The residue was redissolved in toluene/acetone (7/3, v/v, 100 mL) and filtered to remove inorganic salts. The solvent was removed under reduced pressure and the residue was suspended in MeOH (20 mL) and filtered. The crude product was purified by flash column chromatography on silica gel (100% CHCl$_3$ (Rf value for **11** in CHCl$_3$ = 0.42). The solvent was removed under reduced pressure and the red coloured solid was dried at 70 ˚C *in vacuo* (60 mbar) to yield **11** (0.40 g, 59%). HRMS: found *m/z* 666.2600 (M+H)$^+$; calculated *m/z* 666.2599. M. pt. found: 150-151 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3091, 2947, 2896, 1722, 1708, 1508, 1245, 1157. UV λ_{max} (0.1 mM in CHCl$_3$): 323 nm (Ɛ = 75,000 cm^{-1} M^{-1}). TGA (Air): Weight loss at 300 °C (1.29%); Onset temperature (326 °C). ^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.31 (t, *J* 7.1 Hz, 6H), 1.93 (s, 3H), 4.35 (q, *J* 7.1 Hz, 4H), 6.63 (d, *J* 2.5 Hz, 1H), 6.68 (dd, *J* 8.9, 2.5 Hz, 1H), 7.43 (m, 2H), 7.50-7.53 (m, 4H), 7.71 (m, 4H), 7.81 (m, 4H), 8.65 (d, *J* 8.9 Hz, 1H), 8.65-8.70 (m, 4H), 13.53 (s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 13.5, 20.33, 62.0, 82.2, 106.0, 110.1, 112.1, 126.8, 127.0, 127.7, 128.5, 129.0, 130.7, 133.7, 139.6, 145.3, 160.2, 163.2, 167.8, 170.7

3-[4-(4,6-Diphenyl-1,3,5-triazin-2-yl)-3-hydroxyphenoxy]-1,2-propanediol (12). A mixture of 4-(4,6-diphenyl-1,3,5-triazin-2-yl)benzene-1,3-diol **5** (1.50 g, 4.39 mmol), Na$_2$CO$_3$ (1.40 g, 13.18 mmol) and KI (1.10 g, 6.59 mmol) in DMF (100 mL) was stirred at 70 °C. To this, a solution of 3-chloropropane-1,2-diol (1.95 g, 17.58 mmol) in DMF (50 mL) was added and stirred at 110 °C for 3 days. The mixture was filtered whilst hot and the solvent removed under reduced pressure. The residue was suspended in water (75 mL) and stirred at room temperature for 30 mins. The solid was collected by filtration and washed with water (50 mL). The crude solid was purified by flash column chromatography on silica gel (10% MeOH in CHCl$_3$, Rf value for **12** in 10% MeOH in CHCl$_3$ = 0.35). The solvent was removed under reduced pressure and the yellow coloured solid was dried at 70 ˚C *in vacuo* (60 mbar) to yield **12** (1.35 g, 75%). HRMS: found *m/z* 416.1611 (M+H)$^+$; calculated *m/z* 416.1605. M. pt. found: 203-205 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3100-3400, 3060, 2954, 2921, 2896, 1511, 1355, 1262. UV λ_{max} (0.1 mM in DMSO): 342 nm (Ɛ = 24,000 cm^{-1} M^{-1}). TGA (Air): Weight loss at 300 °C (2.26%); Onset temperature (312 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 3.48 (m, 2H), 3.80-3.87 (m, 1H), 3.93-3.97 (m, 1H), 4.07-4.11 (m, 1H), 4.72 (t, *J* 5.7 Hz, 1H), 5.02 (d, *J* 5.2 Hz, 1H), 6.50 (d, *J* 2.5 Hz, 1H), 6.62 (dd, *J* 9.0, 2.5 Hz, 1H), 7.63-7.66 (m, 4H), 7.72 (m, 2H), 8.52-8.56 (m, 5H), 13.31 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 62.5, 69.8, 70.0, 101.7, 108.3, 109.9, 128.5, 129.1, 131.1, 133.3, 134.6, 163.7, 164.8, 169.6, 170.5.

3-(4-(4,6-*Bis*(4-methoxyphenyl)-1,3,5-triazin-2-yl)-3-hydroxyphenoxy)propane-1,2-diol (13). A mixture of 4-(4,6-*bis*(4-methoxyphenyl)-1,3,5-triazin-2-yl)benzene-1,3-diol **6** (0.25 g, 0.62 mmol), Na$_2$CO$_3$ (0.23 g, 2.18 mmol) and KI (0.16 g, 0.90 mmol) in DMF (20 mL) was stirred at 70 °C. To this, a solution of 3-chloropropane-1,2-diol

(0.31 g, 2.80 mmol) in DMF (5 mL) was added and stirred at 110 °C for 7 days. The mixture was filtered whilst hot and more than 50% of the solvent removed under reduced pressure. 5% v/v Aqueous HCl (50 mL) was added to the residue and the precipitate collected by filtration, washing with deionized water (50 mL). The crude solid was purified by flash column chromatography on silica gel (10% MeOH in $CHCl_3$, Rf value for **13** in 10% MeOH in $CHCl_3$ = 0.33). The solvent was removed under reduced pressure and the red coloured solid was dried at 70 ˚C *in vacuo* (60 mbar) to yield **13** (0.19 g, 64%). HRMS: found *m/z* 476.1821 $(M+H)^+$; calculated *m/z* 476.1816. M. pt. found: 182-185 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3050-3400, 3030, 2954, 2928, 2837, 1504, 1256, 1174. UV λ_{max} (0.1 mM in DMSO): 321 nm (Ɛ = 55,000 cm^{-1} M^{-1}). TGA (Air): Weight loss at 300 °C (5.66%); Onset temperature (310 °C). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ: 3.47-3.51 (m, 2H), 3.84-3.86 (m, 1H), 3.88 (s, 6H), 3.93-3.97 (m, 1H), 4.07-4.11 (m, 1H), 4.71 (t, *J* 5.3 Hz, 1H), 5.01 (d, *J* 4.9 Hz, 1H), 6.49 (d, *J* 2.4 Hz, 1H), 6.62 (dd, *J* 8.9, 2.4 Hz, 1H), 7.12 (d, *J* 7.1 Hz, 4H), 8.41-8.47 (m, 5H), 13.41 (s, 1H). ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ: 56.0, 63.1, 70.3, 70.5, 102.2, 108.5, 110.6, 114.9, 127.4, 131.0, 131.5, 163.9, 164.1, 165.0, 169.3, 170.6.

3-(4-(4,6-*Bis*(4-fluorophenyl)-1,3,5-triazin-2-yl)-3-hydroxyphenoxy)propane-1,2-diol (14). A mixture of 4-(4,6-*bis*(4-fluorophenyl)-1,3,5-triazin-2-yl)benzene-1,3-diol **7** (1.00 g, 2.65 mmol), KI (0.68 g, 4.10 mmol) and Na_2CO_3 (0.84 g, 7.93 mmol) in DMF (75 mL) was stirred at 70 °C. To this, a solution of 3-chloropropane-1,2-diol (1.16 g, 10.49 mmol) in DMF (25 mL) was added and stirred at 110 °C for 16 hours. The mixture was filtered whilst hot and the solvent removed under reduced pressure. DMF (5 mL) was added to the residue followed by 5% v/v aqueous HCl (50 mL). The precipitate was collected by filtration and washed with water (40 mL). The crude solid was purified by flash column chromatography on silica gel (10% MeOH in $CHCl_3$, Rf value for **14** in 10% MeOH in $CHCl_3$ = 0.37). The solvent was removed under reduced pressure and the yellow coloured solid was dried at 70 ˚C *in vacuo* (60 mbar) to yield **14** (0.84 g, 70%). HRMS: found *m/z* 450.1278 $(M-H)^-$; calculated *m/z* 450.1271. M. pt. found: 182-185 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3100-3400, 2932, 1530, 1504, 1264, 1236, 1227. UV λ_{max} (0.1 mM in DMSO): 342 nm (Ɛ = 21,000 cm^{-1} M^{-1}). TGA (Air): Weight loss at 300 °C (4.07%); Onset temperature (319 °C). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ: 3.48 (m, 2H), 3.82-3.87 (m, 1H), 3.91-3.95 (m, 1H), 4.05-4.08 (m, 1H), 4.74 (t, *J* 5.6 Hz, 1H), 5.04 (d, *J* 5.1 Hz, 1H), 6.41 (d, *J* 2.4 Hz, 1H), 6.56 (dd, *J* 9.0, 2.4 Hz, 1H), 7.35-7.39 (m, 4H), 8.35 (d, *J* 9.0 Hz, 1H), 8.34-8.45 (m, 4H), 12.99 (s, 1H). ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ: 62.6, 69.8, 70.0, 101.6, 108.1, 109.7, 116.0 (d, *J* 22 Hz), 130.8 (d, *J* 3 Hz), 131.1 (d, *J* 9 Hz), 132.4, 163.6, 164.8, 165.0 (d, *J* 254 Hz), 168.3, 170.3. ^{19}F NMR (400 MHz, DMSO) δ: -106.2 (m, 2F).

3-[4-(4,6-Diphenyl-1,3,5-triazin-2-yl)-3,5-dihydroxyphenoxy]-1,2-propanediol (15). A mixture of 4-(4,6-diphenyl-1,3,5-triazin-2-yl)benzene-1,3-diol **8** (1.50 g, 4.20 mmol), Na_2CO_3 (1.55 g, 14.70 mmol) and KI (1.22 g, 7.36 mmol) in DMF (100 mL) was stirred at 70 °C. To this, a solution of 3-chloropropane-1,2-diol (2.09 g, 18.9 mmol) in DMF (50 mL) was added and stirred at 110 °C for 5 days. The mixture was filtered whilst hot and the solvent removed under reduced pressure. The residue was suspended in 10% v/v aqueous HCl (50 mL) and stirred at room temperature for 30 mins. The solid was collected by filtration and washed with water (50 mL). The crude solid was dissolved in hot DMF (10 mL) and cooled to room temperature. To this, MeOH (70 mL) was added to form a precipitate which was collected by filtration and washed with MeOH (30 mL). The red coloured solid was dried at 70 °C *in vacuo* (60 mbar) to yield **15** (1.23 g, 68%). HRMS: found *m/z* 432.1560 $(M+H)^+$; calculated *m/z* 432.1554. M. pt. found: 236-238 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3100-3500, 3058, 2900, 1511, 1152. UV λ_{max} (0.1 mM in DMSO): 327 nm (Ɛ = 34,000 cm^{-1} M^{-1}). TGA (Air): Weight loss at 300 °C (3.61%); Onset temperature (329 °C). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ: 3.46 (d, *J* 5.5 Hz, 2H), 3.78-3.81 (m, 1H), 3.86-3.90 (m, 1H), 4.01-4.04 (m, 1H), 4.71 (s, 1H), 4.99 (s, 1H), 6.00 (s, 2H), 7.63-7.67 (m, 4H), 7.74 (m, 2H), 8.36 (m, 4H), 13.53 (s, 2H). ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ: 62.6, 69.7, 70.0, 94.5, 96.6, 128.5, 129.3, 133.7, 133.8, 164.0, 165.3, 168.4, 170.5.

3-{4-[4,6-*Bis*(4-biphenylyl)-1,3,5-triazin-2-yl]-3,5-dihydroxyphenoxy}-1,2-propanediol (16). A mixture of 4-(4,6-di([1,1′-biphenyl]-4-yl)-1,3,5-triazin-2-yl)benzene-1,3-diol **9** (0.25 g, 0.51 mmol), Na_2CO_3 (0.16 g, 1.52 mmol) and KI (0.13 g, 0.77 mmol) in DMF (10 mL) was stirred at 70 °C. To this, a solution of 3-chloropropane-1,2-diol (0.23 g, 2.04 mmol) in DMF (5 mL) was added and stirred at 110 °C for 3 days. The mixture was filtered whilst hot and the solvent was removed under reduced pressure. The residue was suspended in 10% v/v aqueous HCl (15 mL) and stirred at room temperature for 30 mins. The solid was collected by filtration and washed with water (30 mL). The crude solid was purified by flash column chromatography on silica gel (10% MeOH in $CHCl_3$, Rf value for **16** in 10% MeOH in $CHCl_3$ = 0.40). The solvent was removed under reduced pressure and the red coloured solid was dried at 70 ˚C *in vacuo* (60 mbar) to yield **16** (0.17 g, 59%). HRMS: found *m/z* 568.2242 $(M+H)^+$; calculated *m/z* 568.2231. M. pt. found: 251-252 ˚C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3000-3600, 3030, 2926, 1506, 1260. UV λ_{max} (0.1 mM in DMSO): 323 nm (Ɛ = 74,000 cm^{-1} M^{-1}). TGA (Air): Weight loss at 300 °C (3.29%); Onset temperature (346 °C). ^1H NMR (500 MHz, DMSO-d_6) δ: 3.47-3.49 (m, 2H), 3.81-3.86 (m, 1H), 3.92-3.95 (m, 1H), 4.05-4.08 (m, 1H), 4.73 (t, *J* 5.6 Hz), 5.02 (d, *J* 5.2 Hz, 1H), 6.47 (d, *J* 2.4 Hz, 1H), 6.61 (dd, *J* 8.9, 2.4 Hz, 1H), 7.43 (m, 2H), 7.48-7.51 (m, 4H), 7.71 (m, 4H), 7.84 (d, *J* 8.5 Hz, 4H), 8.44 (d, *J* 8.9 Hz, 1H), 8.59 (d, *J* 8.5 Hz, 4H), 13.24 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 63.1, 70.3, 70.4, 102.1, 108.6, 110.4, 127.4, 127.6, 128.8, 129.5, 130.0, 131.5, 133.9, 139.4, 145.1, 164.1, 165.2, 169.6, 170.9.

2-(4,6-*Bis*(4-methoxyphenyl)-1,3,5-triazin-2-yl)-5-(2-hydroxyethoxy)phenol (17). A solution of 4-(4,6-*bis*(4-methoxyphenyl)-1,3,5-triazin-2-yl)benzene-1,3-diol **6** (0.25 g, 0.62 mmol) and Na_2CO_3 (0.13 g, 1.25 mmol) in DMF (20 mL) was stirred at 70 ˚C. To this, a solution of 2-bromoethanol (0.16 g, 1.25 mmol) in DMF (5 mL) was added and the mixture was stirred at 110 ˚C for 16 hours. The reaction mixture was filtered whilst hot and the solvent was removed under reduced pressure. The residue was suspended in water (30 mL), stirred for 1 hour at room temperature and filtered. The brown coloured solid was resuspended in acetone (5 mL), collected by filtration and washed with acetone (10 mL). The beige coloured solid was dried overnight at 70 ˚C *in vacuo* (60 mbar) to yield **17** (0.17 g, 61%). HRMS: found *m/z* 446.1716 $(M+H)^+$; calculated *m/z* 446.1721**.** M. pt. found: 121-123 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3100-3400, 3005, 2931, 2835, 1500, 1251, 1170**.** UV λ_{max} (0.1 mM in DMSO): 322 nm (Ɛ = 61,000 cm^{-1} M^{-1}). TGA (Air): Weight loss at 300 °C (1.71%); Onset temperature (339 °C). ^1H NMR (400 MHz, DMSO-d_6) δ: 3.72-3.75 (m, 2H), 3.87 (s, 6H), 4.04 (t, *J* 4.8 Hz, 2H), 4.91 (t, *J* 5.2 Hz, 1H), 6.47 (d, *J* 2.3 Hz, 1H), 6.59 (dd, *J* 9.0, 2.3 Hz, 1H), 7.10 (d, *J* 8.9 Hz, 4H), 8.39-8.44 (m, 5H), 13.4 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 55.5, 59.4, 69.9, 101.5, 107.9, 110.0, 114.3, 126.9, 130.4, 130.9, 163.3, 163.6, 164.4, 168.6, 170.0.

2-(4,6-*Bis*(4-fluorophenyl)-1,3,5-triazin-2-yl)-5-(2-hydroxyethoxy)phenol (18). A mixture of 4-(4,6-*bis*(4-fluorophenyl)-1,3,5-triazin-2-yl)benzene-1,3-diol **7** (0.25 g, 0.66 mmol) and Na_2CO_3 (0.14 g, 1.32 mmol) in DMF (20 mL) was stirred at 70 °C. To this, a solution of 2-bromoethanol (0.17 g, 1.32 mmol) in DMF (5 mL) was added and stirred at 110 °C for 16 hours. The mixture was filtered whilst hot and the solvent was removed under reduced pressure. DMF (5 mL) was added to the residue followed by 5% v/v aqueous HCl (50 mL), and the precipitate was collected by filtration, washing with water (40 mL). The crude solid was purified by flash column chromatography on silica gel (10% MeOH in $CHCl_3$, Rf value for **18** in 10% MeOH in $CHCl_3$ = 0.38) and the solvent was removed under reduced pressure. The yellow coloured solid was dried at 70 ˚C *in vacuo* (60 mbar) to yield **18** (0.23 g, 83%). HRMS: found *m/z* 420.1175 $(M-H)^-$; calculated *m/z* 420.1165. M. pt. found: 220-222 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3150-3450, 3081, 2934, 1506, 1260. UV λ_{max} (0.1 mM in DMSO): 345 nm (Ɛ = 19,000 cm^{-1} M^{-1}). TGA (Air): Weight loss at 300 °C (8.59%); Onset temperature (309 °C). ^1H NMR (400 MHz, DMSO-d_6) δ: 3.74-3.76 (m, 2H), 4.04 (t, *J* 4.8 Hz, 2H), 4.92 (s, 1H), 6.45 (d, *J* 2.5 Hz, 1H), 6.57 (dd, *J* 9.0, 2.5 Hz, 1H), 7.37-7.42 (m, 4H), 8.40 (d, *J* 9.0 Hz, 1H), 8.47-8.51 (m, 4H), 13.02 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 59.4, 69.9, 101.5, 108.1, 109.7, 116.0 (d, *J* 22Hz, 130.8, 131.1 (d, *J* 9 Hz), 132.4, 163.6, 164.7, 165.0 (d, *J* 254 Hz), 168.3, 170.3. ^{19}F NMR (400 MHz, DMSO) δ: -106.3 (m, 2F).

2-(4,6-Diphenyl-1,3,5-triazin-2-yl)-5-(2-hydroxyethoxy)benzene-1,3-diol (19). A solution of 2-(4,6-diphenyl-1,3,5-triazin-2-yl)benzene-1,3,5-triol **8** (3.00 g, 8.40 mmol) and Na_2CO_3 (1.78 g, 16.80 mmol) in DMF (100 mL) was stirred at 70 ˚C. To this, a solution of 2-bromoethanol (2.10 g, 16.80 mmol) in DMF (50 mL) was added and the mixture was stirred at 110 ˚C for 16 hours. The mixture was filtered whilst hot and the solvent was removed under reduced pressure. The residue was suspended in water (100 mL), ultrasonicated for 10 mins and stirred at room temperature for 30 mins. The solid was collected by filtration and washed with water (100 mL). The light yellow coloured solid was dried overnight at 70 ˚C *in vacuo* (60 mbar) to yield **19** (3.20 g, 95%). HRMS: found *m/z* 402.1452 $(M+H)^+$; calculated *m/z* 402.1448. M. pt. found: 245-248 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3150-3400, 2931, 2875, 1537, 1514, 1330, 1172. UV λ_{max} (0.1 mM in DMSO): 327 nm (Ɛ = 33,000 cm^{-1} M^{-1}). TGA (Air): Weight loss at 300 °C (5.65%); Onset temperature (314 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 3.69-3.71 (m, 2H), 3.96 (t, *J* 4.9 Hz, 2H), 4.89 (t, *J* 5.5 Hz, 1H), 5.98 (s, 2H), 7.63-7.66 (m, 4H), 7.72 (t, *J* 7.3 Hz, 2H), 8.34 (d, *J* 7.3 Hz, 4H), 13.51 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 59.8, 70.3, 95.0, 97.1, 129.0, 129.8, 134.2, 134.3, 164.5, 165.8, 168.9, 171.0.

2,4-Dichloro-6-phenyl-1,3,5-triazine (20). 1 M Phenylmagnesium bromide in THF (110 mL, 11.00 mmol) was added dropwise to a solution of cyanuric chloride (20.00 g, 10.84 mmol) in anhydrous THF (300 mL) under nitrogen, whilst maintaining the temperature at 0 °C. Once the addition was complete, the mixture was stirred at 0 °C for 4 hours and poured into 10% v/v aqueous HCl (200 mL). The THF was removed under reduced pressure and the organic product was extracted with $CHCl_3$ (3×150 mL). The organic layer was combined and washed with water (2×150 mL) and brine (100 mL), dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by grinding into a fine powder, suspending and washing with MeOH (3×100 mL). This yielded a white powder which was dried at 70 °C *in vacuo* (60 mbar) to yield **20** (15.67 g, 64%). HRMS: found *m/z* 226.0121 $(M+H)^+$; calculated *m/z* 225.9933. M. pt. expected: 118-120 °C;[43] found: 118-120 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3030, 1523, 1494. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52-7.56 (**m**, 2H), 7.65-7.69 (**m**, 1H), 8.50-8.52 (**m**, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 129.3, 130.1, 132.9, 134.9, 172.3, 175.1.

2,4-Dichloro-6-(4-methoxyphenyl)-1,3,5-triazine (21). 0.5 M 4-Methoxyphenylmagnesium bromide in THF (20 mL, 10.00 mmol) was added to a stirred solution of cyanuric chloride (1.84 g, 10.00 mmol) in anhydrous THF (25 mL) under nitrogen, whilst maintaining the temperature at 0 °C. Once the addition was complete, the reaction mixture was stirred at 0 °C for 4 hours and then poured into cold 10% v/v aqueous HCl (50 mL). The THF was removed under reduced pressure and the organic product was extracted with $CHCl_3$ (2×50 mL). The organic layer was washed with water (2×100 mL), brine (100 mL), dried over anhydrous sodium sulfate and the solvent removed under reduced pressure. The crude solid was purified by grinding into a fine powder, suspending and washing with MeOH (3×100 mL). The white coloured product was dried at 40 ˚C *in vacuo* (60 mbar) to yield **21** (1.20 g, 47%). HRMS: found *m/z* 256.0036 $[M]^+$; calculated *m/z* 256.0039. M. pt. expected: 137-138 °C;[44] found: 137-138 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3078, 2974, 2937, 1516, 1477, 1244. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.92 (s, 3H), 7.01 (d, *J* 9.1 Hz, 2H), 8.47 (d, *J* 9.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.7, 114.5, 125.1, 132.3, 165.2, 171.6, 174.2.

4,4'-(6-Phenyl-1,3,5-triazine-2,4-diyl)bis(benzene-1,3-diol) (22). A mixture of 2,4-dichloro-6-phenyl-1,3,5-triazine **20** (8.00 g, 0.035 mol) and resorcinol (7.99. g, 0.073 mol) in anhydrous 1,2-dichloroethane (250 mL) was warmed to 70 °C under nitrogen. Once the resorcinol had dissolved, the reaction mixture was cooled to 40 °C and $AlCl_3$ (9.68 g, 0.073 mol) was added. The mixture was heated to 55 °C, and a dark red coloured precipitate formed after 1 hour which prevented stirring. The reaction was kept at 55 °C without stirring for a further 16 hours. The mixture was cooled to room temperature, water (200 mL) was added and the supernatant removed. The solid residue remaining in the reaction flask was suspended in hot MeOH/water (50/50, v/v, 250 mL) and ultrasonicated at 55 °C for 1 hour. The yellow coloured solid was collected by filtration and washed with MeOH

(100 mL) and dried at 70 °C *in vacuo* (60 mbar) to yield **22** (8.97 g, 68%). No further purification was necessary and the yellow coloured crude solid was used in the subsequent step. HRMS: found *m/z* 374.1132 $(M+H)^+$; calculated *m/z* 374.1135. M. pt. found: 335-338 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3200-3350, 3020, 1508, 1101. UV λ_{max} (0.1 mM in DMSO): 352 nm (Ɛ = 36,000 cm^{-1} M^{-1}). TGA (Air): Weight loss at 300 °C (0.27%); Onset temperature (415 °C). ^{1}H NMR (500 MHz, DMSO) δ: 6.36 (d, *J* 2.3 Hz, 2H), 6.51 (dd, *J* 8.8, 2.3 Hz, 2H), 7.62-7.65 (m, 2H), 7.71 (t, *J* 7.3 Hz, 1H), 8.27 (d, *J* 8.8 Hz, 2H), 8.33 (d, *J* 7.3 Hz, 2H), 10.49 (s, 2H), 13.03 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ: 103.6, 109.3, 109.4, 128.7, 129.7, 131.9, 133.8, 134.8, 164.2, 164.8, 168.3, 169.8.

4,4'-(6-(4-Methoxyphenyl)-1,3,5-triazine-2,4-diyl)bis(benzene-1,3-diol) (23). $AlCl_3$ (1.19 g, 8.92 mmol) was added to a solution of 2,4-dichloro-6-(4-methoxyphenyl)-1,3,5-triazine **21** (1.00 g, 3.90 mmol) and resorcinol (0.99 g, 9.00 mmol) in 1,2-dichlorobenzene (25 mL) and the mixture was stirred at 130 °C for 1 hour under nitrogen. A precipitate formed which was broken up using a glass rod and the reaction mixture was stirred at 130 °C for 16 hours. The mixture was cooled to room temperature, 10% v/v aqueous HCl (30 mL) was added and stirred for 30 mins. The suspension was spun in a centrifuge (2000 rpm, 2 mins) and the supernatant was removed. The residue was resuspended in water (30 mL), spun in a centrifuge (2000 rpm, 2 mins) and the supernatant was removed. The solid residue was collected by filtration, washed with water (100 mL) and dried at 70 °C *in vacuo* (60 mbar). The crude brown coloured solid was purified by dissolving in hot DMF (10 mL) and precipitating the product with cold water (20 mL). The precipitate was collected by filtration, washed with water (100 mL) and the yellow coloured solid was dried at 70 °C *in vacuo* (60 mbar) to yield **23** (1.12 g, 71%). HRMS: found *m/z* 404.1245 $(M+H)^+$; calculated *m/z* 404.1241. M. pt. found: >360 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 2900-3600, 3022, 2850, 1506, 1165. UV λ_{max} (0.1 mM in DMSO): 343 nm (Ɛ = 46,000 cm^{-1} M^{-1}). TGA (Air): Weight loss at 300 °C (3.17%); Onset temperature (354 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 3.88 (s, 3H), 6.36 (d, *J* 2.3 Hz, 2H), 6.50 (dd, *J* 8.8, 2.3 Hz, 2H), 7.16 (d, *J* 9.0 Hz, 2H), 8.23-8.28 (m, 4H), 10.46 (s, 2H), 13.35 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 55.6, 103.1, 108.78, 108.82, 114.6, 126.2, 130.2, 131.2, 163.6, 163.7, 164.2, 167.1, 169.1.

6,6’-(6-Phenyl-1,3,5-triazine-2,4-diyl)bis(3-(2-hydroxyethoxy)phenol) (24). A mixture of 4,4'-(6-phenyl-1,3,5-triazine-2,4-diyl)bis(benzene-1,3-diol) **22** (3.00 g, 8.04 mmol) and Na_2CO_3 (4.26 g, 40.20 mmol) in DMF (200 mL) was heated to 70 °C whilst stirring. A solution of 2-bromoethanol (2.50 g, 20.00 mmol) in DMF (100 mL) was added slowly. Once the addition was complete, the mixture was stirred at 110 °C for 16 hours. The mixture was cooled to 70 °C and a second solution of 2-bromoethanol (2.50 g, 20.00 mmol) in DMF (100 mL) was added dropwise. Once the addition was complete, the mixture was stirred at 110 °C for an additional 16 hours. The mixture was filtered whilst hot, the solvent removed under reduced pressure and the residue was redissolved in ethyl acetate/MeOH (8/2, v/v, 100 mL). The organic layer was washed with 5% v/v aqueous acetic acid (50 mL), 0.25 M aqueous $NaHCO_3$ (50 mL) and brine (50 mL). The organic layer was dried using sodium sulfate and the solvent removed under reduced pressure. The light yellow solid was suspended in MeOH (25 mL), filtered and dried at 70 °C *in vacuo* (60 mbar) to yield **24** (1.50 g, 41%). HRMS: found *m/z* 462.1660 $(M+H)^+$; calculated *m/z* 462.1660. M. pt. found: 222-225 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3150-3400, 2921, 2879, 1537, 1508, 1290, 1232. UV λ_{max} (0.1 mM in DMSO): 349 nm (Ɛ = 37,000 cm^{-1} M^{-1}). TGA (Air): Weight loss at 300 °C (1.74%); Onset temperature (388 °C). ^{1}H NMR (400 MHz, DMSO) δ: 3.73-3.77 (m, 4H), 4.06 (t, *J* 4.8 Hz, 4H), 4.93 (t, *J* 5.6 Hz, 2H), 6.51 (d, *J* 2.4 Hz, 2H), 6.62 (dd, *J* 9.0, 2.4 Hz, 2H), 7.63-7.67 (m, 2H), 7.73 (m, 1H), 8.31-8.36 (m, 4H), 13.03 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ: 59.3, 69.9, 101.8, 108.2, 109.8, 128.1, 129.2, 131.0, 133.4, 134.1, 163.5, 164.7, 167.8, 169.1.

6,6'-(6-Phenyl-1,3,5-triazine-2,4-diyl)bis(3-((9-hydroxynonyl)oxy)phenol) (25). A mixture of 4,4'-(6-phenyl-1,3,5-triazine-2,4-diyl)bis(benzene-1,3-diol) **22** (2.00 g, 5.40 mmol) and Na_2CO_3 (2.27 g, 21.60 mmol) in DMF (150 mL) was heated to 70 °C whilst stirring. A solution of 9-bromo-1-nonanol (3.01 g, 13.50 mmol) in DMF (100 mL) was added slowly. Once the addition was complete, the mixture was stirred at 110 °C for 16 hours. The mixture was filtered whilst hot, the solvent removed under reduced pressure and the residue was redissolved in $CHCl_3$ (100 mL). The organic layer was washed with 5% v/v aqueous acetic acid (30 mL), 0.25 M aqueous $NaHCO_3$ (30 mL) and brine (50 mL). The organic layer was dried over sodium sulfate and the solvent removed under reduced pressure. The crude product was suspended in MeOH (25 mL), filtered and dried at 70 °C *in vacuo* (60 mbar). The crude product was purified by flash column chromatography on silica gel (100% $CHCl_3$, switching to 10% MeOH, Rf value for **25** in 10% MeOH in $CHCl_3$ = 0.8). The solvent was removed under reduced pressure and the yellow coloured solid was dried at 70 ˚C *in vacuo* (60 mbar) to yield **25** (1.01 g, 28%). HRMS: found *m/z* 658.3851 $(M+H)^+$; calculated *m/z* 658.3851. M. pt. found: 128-130 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3100-3500, 2922, 2850, 1504, 1533, 1504, 1290, 1234. UV λ_{max} (0.1 mM in $CHCl_3$): 357 nm (ε = 37,000 cm^{-1} M^{-1}). TGA (Air): Weight loss at 300 °C (0%); Onset temperature (411 °C). ^1H NMR (500 MHz, $CDCl_3$) δ: 1.36-1.62 (m, 26H), 1.78-1.83 (m, 4H), 3.64-3.67 (t, *J* 6.8 Hz, 4H), 3.99 (t, *J* 6.6 Hz, 4H), 6.46 (d, *J* 2.4 Hz, 2H), 6.52 (dd, *J* 9.0, 2.4 Hz, 2H), 7.53-7.56 (m, 2H), 7.62 (m, 1H), 8.35 (broad s, 4H), 13.38 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.7, 26.0, 29.3, 29.4, 29.5, 29.1, 32.8, 63.1, 68.3, 101.8, 108.6, 110.0, 128.7, 129.0, 131.2, 133.3, 134.3, 164.6, 165.5. No signals for triazine carbons.

6,6'-(6-(4-Methoxyphenyl)-1,3,5-triazine-2,4-diyl)*bis*(3-(2-hydroxyethoxy)phenol) (26). A solution of 4,4'-(6-(4-methoxyphenyl)-1,3,5-triazine-2,4-diyl)*bis*(benzene-1,3-diol) **23** (0.25 g, 0.62 mmol) and Na_2CO_3 (0.20 g, 1.86 mmol) in DMF (15 mL) was stirred at 70 °C. To this, a solution of 2-bromoethanol (0.23 g, 1.86 mmol) in DMF (5 mL) was added and the reaction mixture was stirred at 110 °C for 16 hours. The mixture was filtered whilst hot and the solvent removed under reduced pressure. The residue was suspended in 10% v/v aqueous HCl (75 mL), ultrasonicated for 20 mins and stirred at room temperature for a further 10 mins. The suspension was spun in a centrifuge (2000 rpm, 2 mins.) and the supernatant removed. The residue was resuspended in water (20 mL), the solid collected by filtration and washed with more water (30 mL). The light brown coloured solid was dried at 70 °C *in vacuo* (60 mbar) to yield **26** (0.20 g, 66%). HRMS: found *m/z* 492.1772 $(M+H)^+$; calculated *m/z* 492.1765. M. pt. expected: 155-158 °C;[44] found: 157-158 °C. FT-IR (ATR): $\bar{\nu}$/ cm^{-1}: 3100-3500, 2935, 1535, 1502, 1255, 1170. UV λ_{max} (0.1 mM in $CHCl_3$): 342 nm (ε = 46,000 cm^{-1} M^{-1}). TGA (Air): Weight loss at 300 °C (1.36%); Onset temperature (331°C). ^1H NMR (400 MHz, DMSO-d_6) δ: 3.73-3.76 (m, 4H), 3.87 (s, 3H), 4.02 (t, *J* 5.7 Hz, 4H), 4.96 (t, *J* 5.5 Hz, 2H), 6.43 (d, *J* 2.4 Hz, 2H), 6.56 (dd, *J* 9.0, 2.4 Hz), 7.11 (d, *J* 9.0 Hz, 2H), 8.15-8.18 (m, 4H), 13.1 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 56.1, 59.9, 70.4, 102.2, 108.6, 108.2, 115.0, 126.6, 130.4, 131.3, 163.7, 164.1, 165.1, 167.6, 169.4.

General Synthesis procedure for Poly(EI-*co*-UVAMs). A stirred slurry of BHEI was pre-heated at 90 °C for 30 mins. Once the viscosity of the slurry had reduced sufficiently, the slurry was poured into a polycondensation (PC) tube. To this, UVAM and Sb_2O_3 (0.15 g, 0.52 mmol) were added and the PC tube was scored lightly on the stem using a Stanley blade, to ensure safe extrusion, and clamped inside a heating block. The PC tube was fitted with a polycondensation head, stirrer guide, air stirrer, delivery side-arm, distillate tube inside an ice-filled Dewar flask, thermocouples and optical revolution counter, and then connected to a gas manifold. The temperature was raised using a control box to 200 °C over 35 mins. under a nitrogen purge. The air stirrer was then started with a pressure of 8.5 psi and the nitrogen purge was then stopped, with the system now under 950 mbar pressure. The pressure was reduced gradually to less than 10 mbar as the temperature was increased to 285-290 °C at a rate of 1 °C/min., with the stirrer speed reaching between 165-175 rpm. After stirring at 285-290 ˚C for 30 mins., the vacuum was slowly replaced with a nitrogen purge. A hammer and chisel were used to break the stem of the PC rig tube, and the copolymer was extruded and quenched into an ice-water bath. The copolymer lace formed was left to dry in air.

A 10% w/v solution of crude polymer in chloroform was filtered through a cotton wool plug and added dropwise into cold methanol, ensuring a 1:10 v/v ratio of chloroform to methanol. The precipitate which formed was filtered and washed with chloroform/methanol (1:10). The precipitate was dried at 40 °C *in vacuo* (60 mbar) for 1 hour and this precipitation process was repeated twice more.

Poly(EI-*co*-10) (P1). DSC: Tg = 66.3 ˚C. GPC: $\overline{M_w}$ = 43,100; $\overline{M_n}$ = 17,200; Đ = 2.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.69 (s, 0.0110H), 6.44 (d, *J* 2.4 Hz, 0.0031H), 6.55 (dd, *J* 8.9, 2.5 Hz, 0.0031H), 4.68 (s, 4H), 7.50 (t, *J* 7.8 Hz, 1H), 8.21 (dd, *J* 7.8, 1.5 Hz, 2H), 8.69 (s, 1H), 13.28 (s, 0.0034H)

Poly(EI-*co*-12) (P2). DSC: Tg = 67.1 ˚C. GPC: $\overline{M_w}$ = 38,500; $\overline{M_n}$ = 14,400; Đ = 2.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.68 (s, 4H), 6.60 (d, *J* 2.5 Hz, 0.0035H), 6.62-6.65 (m, 0.0037H), 7.50 (t, *J* 7.8 Hz, 1H), 8.21 (dd, *J* 7.8, 1.7 Hz, 2H), 8.69 (s, 1H), 13.46 (s, 0.0042H)

Poly(EI-*co*-13) (P3). DSC: Tg = 65.8 ˚C. GPC: $\overline{M_w}$ = 55,000; $\overline{M_n}$ = 14,200; Đ = 3.9. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.68 (s, 4H), 6.58 (d, *J* 2.2 Hz, 0.0024H), 6.62 (dd, *J* 9.0, 2.2 Hz, 0.0024H), 7.50 (t, *J* 7.8 Hz, 1H), 8.21 (dd, *J* 7.8, 1.7 Hz, 2H), 8.69 (s, 1H), 13.69 (s, 0.0036H)

Poly(EI-*co*-14) (P4). DSC: Tg = 66.6 ˚C. GPC: $\overline{M_w}$ = 51,000; $\overline{M_n}$ = 11,800; Đ = 4.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.68 (s, 4H), 6.58 (d, *J* 2.4 Hz, 0.0040H), 6.62-6.65 (m, 0.0039H) 7.50 (t, *J* 7.8 Hz, 1H), 8.21 (dd, *J* 7.8, 1.6 Hz, 2H), 8.69 (s, 1H), 13.33 (s, 0.0056H)

Poly(EI-*co*-15) (P5). DSC: Tg = 67.5 ˚C. GPC: $\overline{M_w}$ = 54,200; $\overline{M_n}$ = 16,000; Đ = 3.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.68 (s, 4H), 6.16 (s, 0.0078H), 7.50 (t, *J* 7.8 Hz, 1H), 8.21 (dd, *J* 7.8, 1.7 Hz, 2H), 8.69 (s, 1H), 13.67 (s, 0.0072H)

Poly(EI-*co*-16) (P6). DSC: Tg = 66.8 ˚C. GPC: $\overline{M_w}$ = 33,300; $\overline{M_n}$ = 12,200; Đ = 2.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.68 (s, 4H), 6.61-6.67 (m, 0.0035H), 7.50 (t, *J* 7.8 Hz, 1H), 8.21 (dd, *J* 7.8, 1.6 Hz, 2H), 8.69 (s, 1H), 13.54 (s, 0.0032H)

Poly(EI-*co*-17) (P7). DSC: Tg = 66.1 ˚C. GPC: $\overline{M_w}$ = 44,900; $\overline{M_n}$ = 12,900; Đ = 3.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.68 (s, 4H, H_4), 6.57 (d, *J* 1.9 Hz, 0.0030H), 6.62 (dd, *J* 7.1, 1.9 Hz, 0.0030H), 7.50 (t, *J* 7.8 Hz, 1H), 8.21 (dd, *J* 7.8, 1.7 Hz, 2H), 8.69 (s, 1H), 13.71 (s, 0.0041H)

Poly(EI-*co*-18) (P8). DSC: Tg = 66.1 ˚C. GPC: $\overline{M_w}$ = 21,000; $\overline{M_n}$ = 7,800; Đ = 2.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.68 (s, 4H), 6.58 (s, 0.0033H), 6.62-6.65 (m, 0.0035H), 7.50 (t, *J* 7.8 Hz, 1H), 8.21 (dd, *J* 7.8, 1.7 Hz, 2H), 8.69 (s, 1H), 13.35 (s, 0.0040H)

Poly(EI-*co*-19) (P9). DSC: Tg = 65.1 ˚C. GPC: $\overline{M_w}$ = 23,700; $\overline{M_n}$ = 7,900; Đ = 3.0. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.68 (s, 4H), 6.16 (s, 0.0060H), 7.50 (t, *J* 7.8 Hz, 1H), 8.21 (d, *J* 7.8 Hz, 2H), 8.69 (s, 1H), 13.63 (s, 0.0068H)

Poly(EI-*co*-24) (P10). DSC: Tg = 68.3 ˚C. GPC: $\overline{M_w}$ = 107,000; $\overline{M_n}$ = 28,500; Đ = 3.8. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.68 (s, 4H), 6.56-6.58 (m 0.0058H) 6.63 (d, *J* 8.0 Hz, 0.0060H), 7.50 (t, *J* 7.8 Hz, 1H), 8.21 (dd, *J* 7.8, 1.7 Hz, 2H), 8.69 (s, 1H), 13.38 (s, 0.0056H)

Poly(EI-*co*-25) (P11). DSC: Tg = 57.6 ˚C. GPC: $\overline{M_w}$ = 45,700; $\overline{M_n}$ = 15,900; Đ = 2.9. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.69 (s, 4H), 6.52-6.60 (m, 0.0062H) 7.51 (s, 1H), 8.21 (s, 2H), 8.70 (s, 1H), 13.43 (s, 0.0030H)

Poly(EI-*co*-26) (P12). DSC: Tg = 69.2 ˚C. GPC: $\overline{M_w}$ = 67,000; $\overline{M_n}$ = 18,100; Đ = 3.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.68 (s, 4H), 6.56 (d, *J* 2.1 Hz, 0.0043H) 6.63 (d, *J* 9.0 Hz, 0.0044H), 7.50 (t, *J* 7.8 Hz, 1H), 8.21 (dd, *J* 7.8, 1.7 Hz, 2H), 8.69 (s, 1H), 13.49 (s, 0.0039H)

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