A Platinum Open Access Journal
for Organic Chemistry

Paper

Free to Authors and Readers

DOAJ Seal

Arkivoc **2023** (ii) 202311993

Facile synthesis of benzotrithiophene core-based hole-transporting molecules with carbazole-wings for perovskite solar cells by Pd-catalyzed direct C-H/C-Br coupling reactions

Wei-Kai Chang,[a] Kun-Mu Lee,*[b] Yin-Chi Wang,[a] Kun-Hua Chiang,[a] Chuan-Pin Lee,[c] and Ching-Yuan Liu*[a]

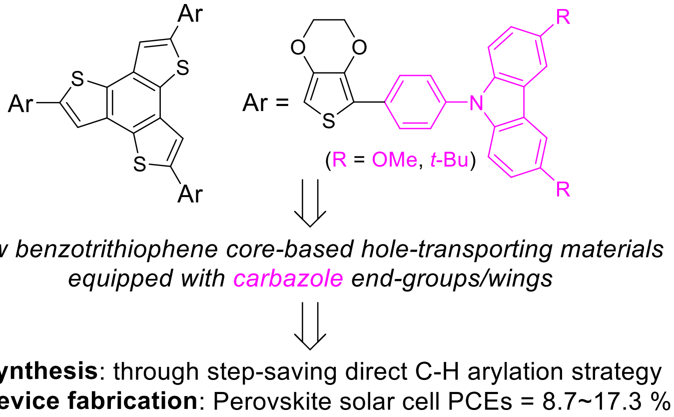
[a] *Department of Chemical and Materials Engineering, National Central University, Jhongli District, Taoyuan City, Taiwan (R.O.C)*
[b] *Department of Chemical and Materials Engineering, Chang Gung University, Guishan District, Taoyuan City, Taiwan (R.O.C)*
[c] *Radioactive Waste Disposal Technology R&D Center, National Tsing Hua University, Hsinchu City, Taiwan (R.O.C)*
Email: cyliu0312@ncu.edu.tw

In Honor of Prof. Tien-Yau Luh

Received 03-29-2023 **Accepted Manuscript** 08-18-2023 **Published on line** 08-27-2023

Abstract

We report herein an efficient synthetic route to two benzotrithiophene core-based hole-transporting materials bearing carbazole end-groups/wings through threefold direct C-H/C-Br cross coupling reactions under optimized Pd-catalysis. Perovskite solar cells employing individual molecule as hole-transport layer exhibited promising power conversion efficiencies of up to 17.30 %. This work provides a step-saving synthetic strategy to access star-shaped new oligoaryls and also expands the substrate scope of end-groups from triphenylamine derivatives to present carbazole-based wings.



Keywords: Benzotrithiophene, Carbazole, Direct C-H arylation, Hole-transporting materials, perovskite solar cells

DOI: https://doi.org/10.24820/ark.5550190.p011.993

Introduction

Application of the direct C-H activation/arylation reactions in the step-saving synthesis of small molecular π-functional organic materials has been emerging as a promising cross-disciplinary research topic for the past two decades.[1-6] For examples, Mori and coworkers reported a series of palladium-catalyzed C-H arylation strategies for the efficient preparation of various organic optoelectronic materials.[7-11] Yorimitsu described a straightforward access to functional small molecules such as aryl-substituted porphyrins and tetrathiafulvalenes via direct C-H arylation reactions.[12-14] Recently Bin and You demonstrated a regioselective C−H/C−H couling protocol as synthesis shourtcut to acesss (benzo)thiophene−containing biaryls for OLED materials.[15] Pasini group has been employing direct arylations as a sustainable approach to synthesize a variety of π-extended functional oligomers.[16-20] Recently, Kim synthesized A−π−D−π−D−π−A-type hole-transporting materials (HTMs) for perovskite solar cells (PSCs) by sequential C−H arylation reactions.[21]

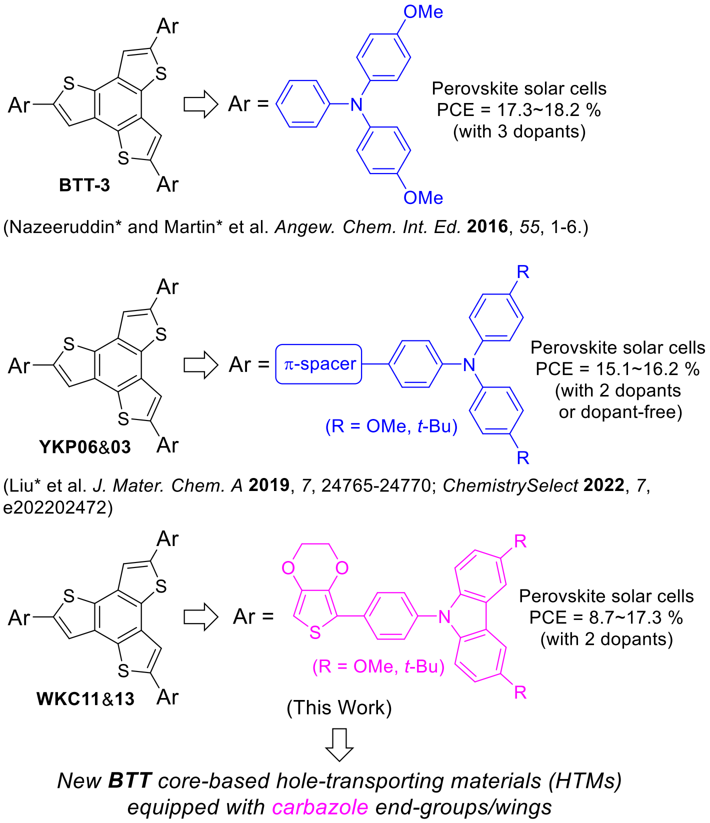
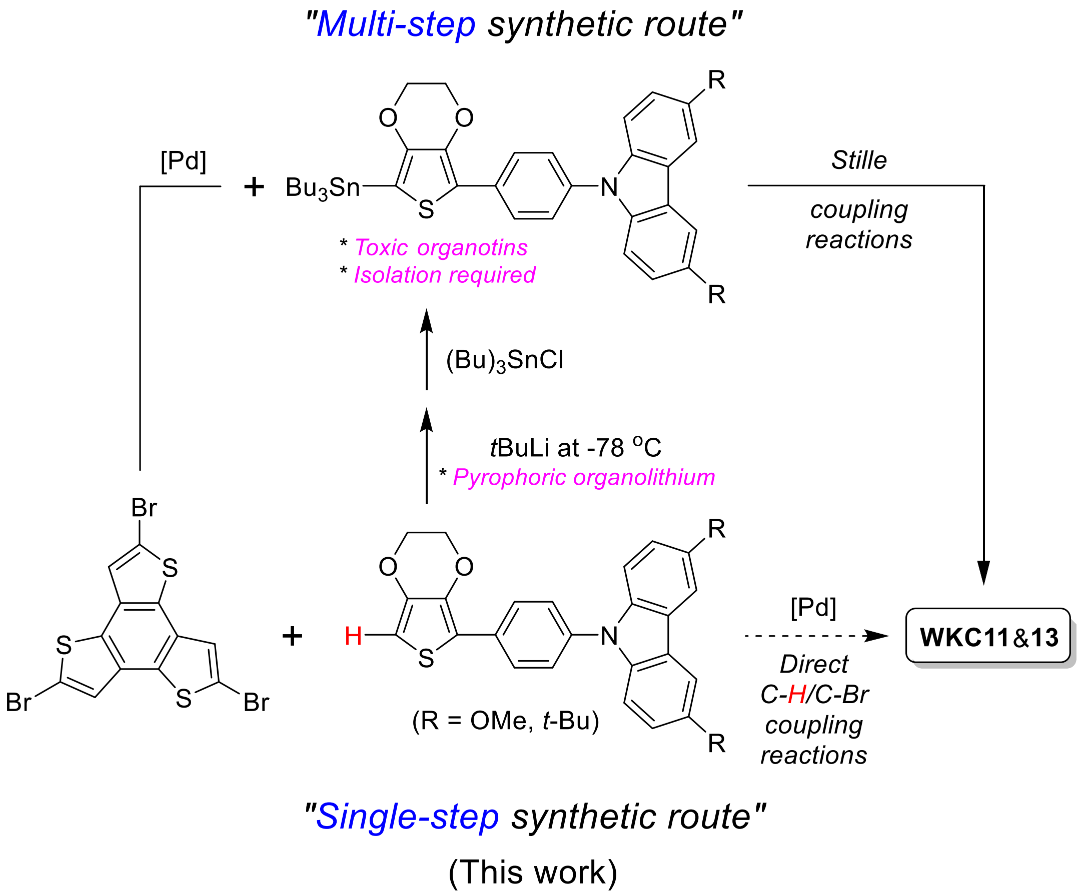


Figure 1. Benzotrithiophene (**BTT**) core-based star-shaped hole-transporting materials: facile synthesis and application in perovskite solar cells.

In addition, since 2014, our group has been endeavouring to develop step-saving new synthetic routes to various π-conjugated small molecules via C-H activation/arylations for optoelectronic applications including dye-sensitized solar cells (DSSCs)[22-26] and new HTM-based perovskite solar cell devices.[27-33] One of our previous work showed an efficient synthesis of benzotrithiophene (**BTT**) core-based oligoaryls bearing triphenylamine end-groups, one of which (**YKP03**) was used as dopant-free and high-performance HTM for stable perovskite solar cells.[31] This result inspired us to design and synthesize **BTT**-based new HTMs. In order to further expand the scope of end-groups, we report herein two star-shaped new HTM molecules bearing carbazole wings (**WKC11** and **WKC13**, Figure 1). To the best of our knowledge, no report on the step-economical synthesis of benzotrithiophene core-based HTMs bearing carbazole wings has appeared to date. Fabrication of **WKC11** or **WKC13** in corresponding perovskite-based solar devices as hole-transport layer displayed promising power conversion efficiency of up to 17.3%.

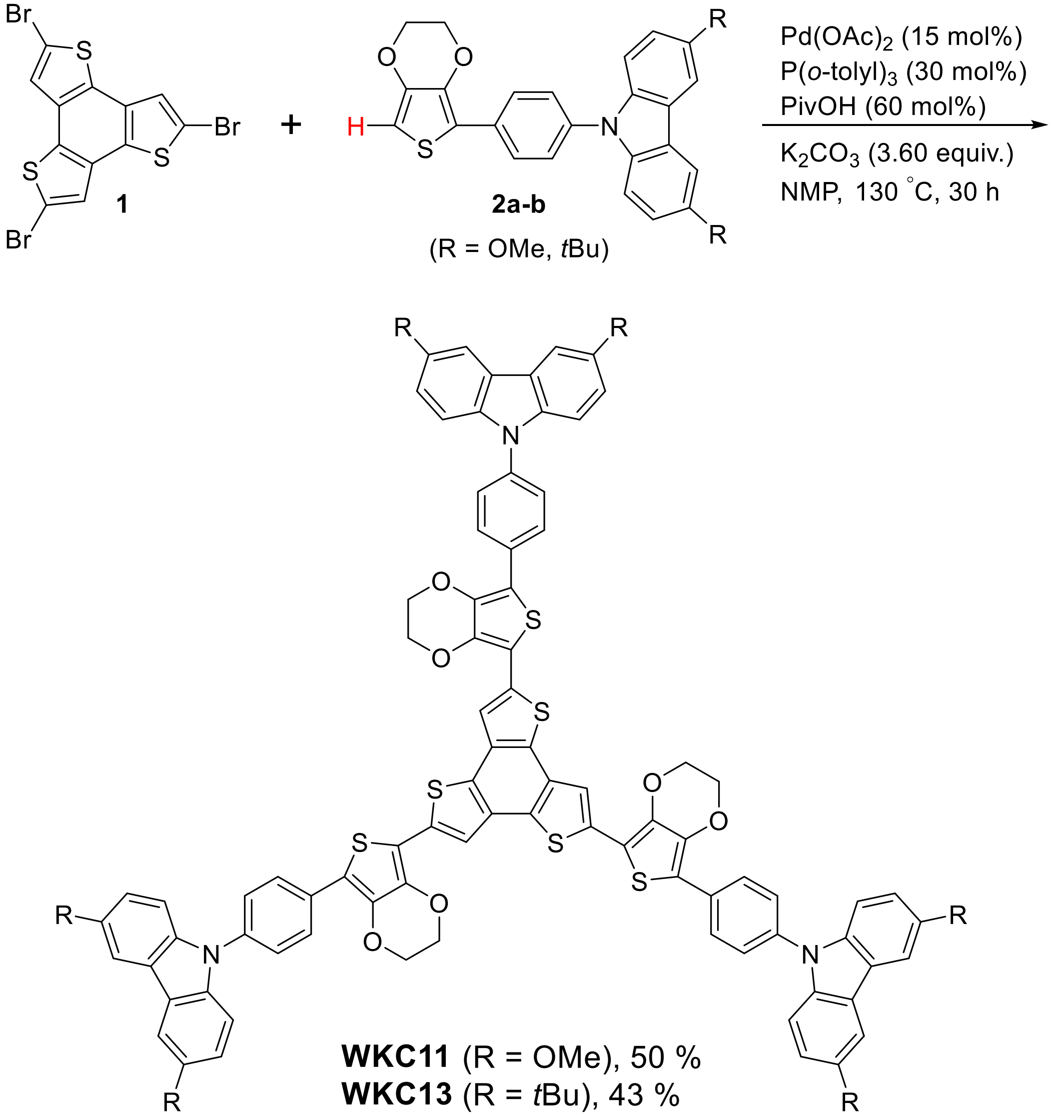
Results and Discussion

Prior to materials synthesis, as shown in Scheme 1, we carried out an analysis in which two synthetic pathways were compared. Traditionally, **WKC11** or **WKC13** are supposed to be prepared using Stille coupling reactions as key transformation. Following the traditional approach is reliable, but it usually requires tedious prefunctionalizations like deprotonations and transmetalations. Additionally, Stille coupling strategy included the use and generation of toxic organotin reagents and their purification was somehow difficult. On the other hand, we proposed herein a step-saving route to efficiently access target **WKC11** or **WKC13** through straightforward C-H/C-Br cross-coupling reactions.



Scheme 1. Synthetic analysis of **WKC11** and **WKC13**: multi-step synthetic route via Stille reaction *vs.* single-step synthetic route via direct C-H arylations.

As shown in Scheme 2, reaction of tribromobenzotrithiophene **1** with the carbazole-containing end-groups **2a**-**b** by Pd-catalyzed threefold direct C-H/C-Br cross-coupling reactions afforded the desired HTMs in moderate isolated yields (**WKC11** = 50%; **WKC13** = 43%). The yields are not satisfactory probably owing to the relatively lower solubility of **WKC11** and **WKC13** in dichloromethane, tetrahydrofuran and acetone, which made the purification processes difficult.



Scheme 2. Synthesis of **WKC11** and **WKC13** using Pd-catalyzed threefold direct C-H/C-Br coupling reaction as key step.

UV/Vis absorption, electrochemistry, thermal stability, and hole mobilities of **WKC11** and **WKC13** were also investigated and the data were summarized in Table 1. **WKC11** and **WKC13** exhibited close optical band-gaps because of their similar conjugation lengths (ΔE_g = 2.73-2.77 eV, calculated by $1240/\lambda_{\text{intersect}}$). By conducting the experiments of cyclic voltammetry, we found that both molecules displayed higher E_{HOMO} (-5.30, -5.34 eV) than that of perovskite layer ($CH_3NH_3PbI_3$, -5.43 eV). This implied **WKC11** and **WKC13** were able to extract holes effectively from $CH_3NH_3PbI_3$. Thermal properties were evaluated by performing thermogravimetric analysis (TGA) and the results revealed that **WKC11** bearing -OMe moieties possessed a superior decomposition temperature (T_d = 385 °C). The hole mobilities of both HTMs were estimated by space-charge-limited currents (SCLCs) in the *J–V* characteristics. **WKC11** exhibited a relatively higher hole mobility (6.13×10^{-4} $cm^2V^{-1}s^{-1}$), which may contribute to higher fill factor and power conversion efficiency.

Table 1. The optical, electrochemical, thermal properties and the hole mobility of **WKC11**and **WKC13** [a-d]

HTM	ΔE_g^{opt} [eV]	E_{HOMO} [eV]	E_{LUMO} [eV]	T_d [°C]	hole mobility [$cm^2V^{-1}s^{-1}$]
WKC11	2.73	-5.30	-2.57	385	6.13×10^{-4}
WKC13	2.77	-5.34	-2.57	316	9.59×10^{-5}

[a] UV-vis absorption spectra and photoluminescence were measured in dichloromethane solution. [b] ΔE_g^{opt} was calculated from the intersection of absorption and PL spectra, $\Delta E_g^{opt} = 1240/\lambda_{intersect}$. [c] $E_{HOMO} = \Delta[E_{1/2\ (vs.\ Fc/Fc^+)} + 5.16]$ eV. [d] $E_{LUMO} = E_{HOMO} + \Delta E_g^{opt}$.

Fabrication and evaluation of perovskite solar cells (PSCs) using **WKC11** or **WKC13** as hole-transport layer were carried out and the obtained photovlotaic parameters were collected in Table 2. PSCs devices based on both HTMs demonstrated good open-circuit voltage: V_{oc} = 1.04 V. However, PSCs with **WKC11** displayed higher short-circuit current: J_{sc} = 21.38 $mAcm^{-2}$ and fill factor: FF = 77.57%, thus leading to a superior power conversion efficiency (PCE) of 17.30% that is close to the PCE of commercially available **spiro-OMeTAD**-based devices.

Table 2. Photovoltaic performances of the perovskite solar cells using **WKC11** and **WKC13** as HTMs[a-c]

HTMs		V_{oc} [V]	J_{sc} [$mAcm^{-2}$]	*FF* [%]	PCE [%]
WKC11(-OMe)	best	1.04	21.38	77.57	17.30
	average	1.04 ± 0.01	20.95 ± 0.38	75.30 ± 1.89	16.39 ± 0.74
WKC13(-*t*Bu)	best	1.04	14.75	57.02	8.72
	average	1.02 ± 0.06	10.34 ± 2.32	62.12 ± 3.34	6.48 ± 1.19
spiro-OMeTAD	best	1.06	23.05	75.84	18.59
	average	0.90 ± 0.12	22.12 ± 0.63	75.35 ± 1.28	17.62 ± 0.75

[a] The statistical data were calculated based on 6-8 cells. [b] Reverse scanning directions. [c] Both HTMs were dopped with two dopants (Li-TFSI: lithium bis(trifluoromethane)sulfonimide and TBP: 4-*tert*-butylpyridine).

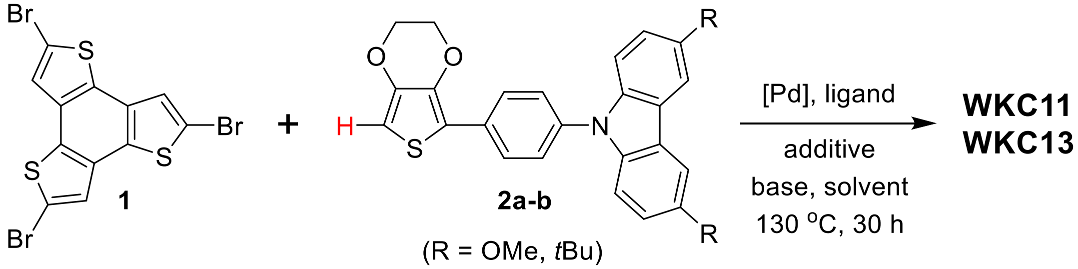
Conclusions

Benzotrithiophene (**BTT**) is a widely used building block in functional organic materials due to its high planarity and simple synthesis. However, further π-extension from **BTT** usually relies on traditional synthetic routes via Stille- or Suzuki coupling reactions, in which the prefunctionalizations are required. This work provides a step-economical synthetic strategy to facilely access new **BTT** core-based hole-transporting materials with carbazole wings (**WKC11** and **WKC13**). Perovskite solar cells using **WKC11** or **WKC13** as hole-transport layer exhibit promising power conversion efficiencies of up to 17.30%.

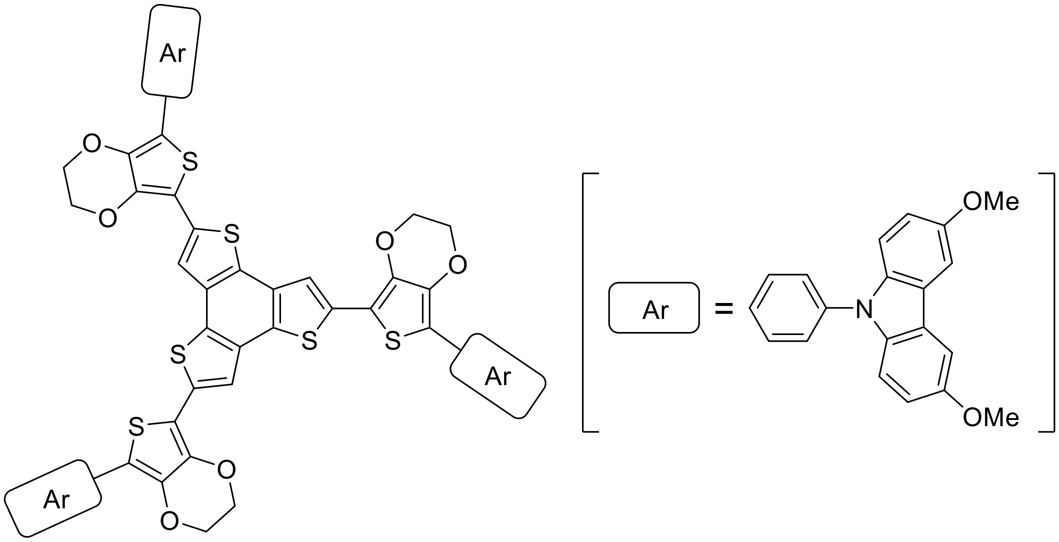
Experimental Section

General. Materials and instruments. Required chemicals such as $Pd(OAc)_2$, P(*o*-tolyl)$_3$, PivOH, and K_2CO_3 are commercially available. Organic solvents such as mesitylene, *N*-methyl-pyrrolidone (NMP), dichloromethane, tetrahydrofuran (THF), hexanes, and acetone were purchased from Sigma-Aldrich, Acros, or Alfa Aesar and used directly without further purifications. NMR spectra were recorded on a Bruker Magnet System 300 or 500 MHz instrument. The mass spectrum recorded by Matrix-Assisted Laser Desorption/Ionization (MALDI) techniques was operated with a Bruker autoflex speed. All details are described in the supplementary material file.

General procedure for the synthesis of **WKC11** and **WKC13**

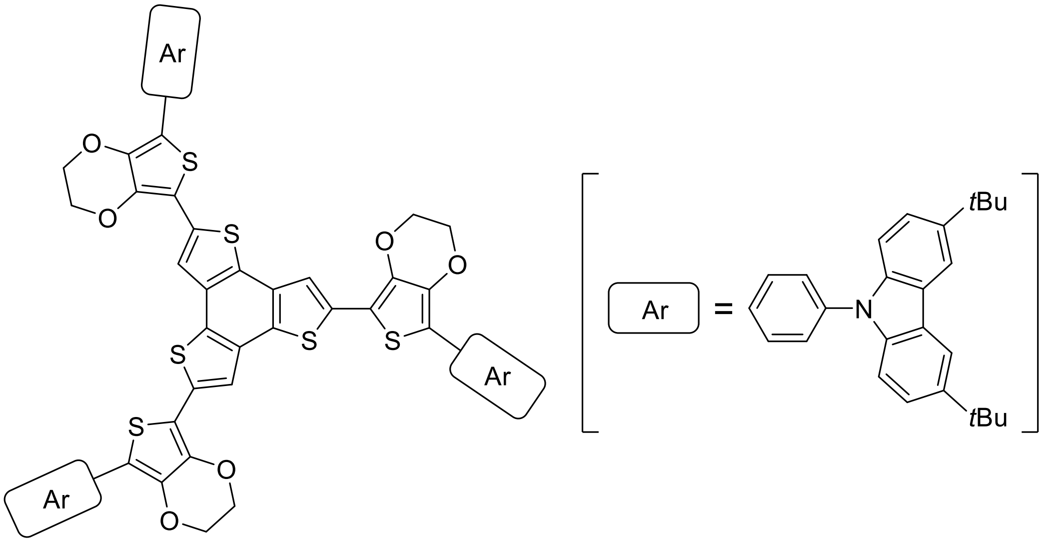


To a solution of $Pd(OAc)_2$ (15 mol %, 10 mg), P(*o*-tolyl)$_3$ (30 mol %, 27 mg), PivOH (60 mol %, 18 mg) and K_2CO_3 (3.60 equiv., 149 mg) in mesitylene or NMP (1.0 mL) in a sealed tube were added the tribromo-**BTT** (**1**) (0.30 mmol) and the corresponding end-groups[30] **2a-b** (1.05 mol) under N_2. The reaction mixture was then heated at 130 °C under N_2 for 30 hours. After the reaction mixture had cooled to room temperature, water (15 mL) was added. The mixture was extracted with dichloromethane (3 × 30 mL), and the combined organic layers were washed with brine (80 mL), dried (Na_2SO_4) and concentrated in *vacuo*. Purification by column chromatography (eluent with a gradient polarity for a better separation: THF : hexanes = 50 : 50, then THF : hexanes = 90 : 10) followed by reprecipitation from acetone afforded the desired products **WKC11** or **WKC13**, respectively.



WKC11 was prepared from trihalogenated **BTT** (**1**) (0.30 mmol) and **2a** (466 mg, 1.05 mmol) according to **General procedure** (reaction conducted in mesitylene) gave the pure product **WKC11** (235 mg, 50%; we

obtained 343 mg as crude product prior to purifications). Yellow solid; mp 264.8-266.3 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.79 (d, *J* 7.5 Hz, 6 H), 7.49 (s, 6 H), 7.43 (s, 3 H), 7.40 (d, *J* 7.5 Hz, 6 H), 7.31 (d, *J* 8.3 Hz, 6 H), 6.96 (d, *J* 8.3 Hz, 6 H), 4.43 (app s, 6 H), 4.30 (app s, 6 H), 3.91 (s, 18 H); ^{13}C NMR (CDCl$_3$, 125 MHz, ppm): δ 154.0, 138.4, 138.3, 136.0, 135.9, 133.3, 131.1, 130.8, 129.3, 126.8, 126.1, 123.6, 116.5, 115.0, 114.3, 111.1, 110.6, 102.9, 64.7, 64.5, 56.0; HRMS (MALDI): calcd. for $C_{90}H_{63}N_3O_{12}S_6$: 1569.2731, found: 1569.2746 (M$^+$).



WKC13 was prepared from trihalogenated **BTT** (**1**) (0.30 mmol) and **2b** (520 mg, 1.05 mmol) according to the **General procedure** (reaction conducted in NMP) gave the pure product **WKC13** (223 mg, 43%; we obtained 353 mg as crude product prior to purifications). Yellow solid; mp >300 °C. ^{1}H NMR (CDCl$_3$, 500 Hz, ppm): δ 8.14 (s, 6 H), 7.89 (d, *J* 6.9 Hz, 6 H), 7.34-7.57 (comp, 21 H), 4.49 (app s, 6 H), 4.36 (app s, 6 H), 1.45 (s, 54 H); ^{13}C NMR (CDCl$_3$, 125 MHz, ppm): δ 143.0, 139.2, 138.6, 136.3, 133.5, 131.5, 130.9, 129.5, 127.1, 126.6, 123.8, 123.6, 116.8, 116.3, 114.5, 111.4, 109.4, 105.1, 64.9, 64.7, 34.8, 32.1; HRMS (MALDI): calcd. for $C_{108}H_{99}N_3O_6S_6$: 1725.5858, found: 1725.5868 (M$^+$).

Acknowledgements

Financial support provided by the Ministry of Science and Technology (MOST), Taiwan (MOST 111-2113-M-008-008 and 108-2628-E-182-003-MY3), National Central University (NCU), Chang Gung University (QZRPD181) and Chang Gung Memorial Hospital, Linkou, Taiwan (CMRPD2M0041) are gratefully acknowledged. We also thank the instrument center (R&D office, NCU, MOST 110-2731-M-008-001) for the technical support of NMR and mass analysis.

Supplementary Material

The data and spectra of mass (MALDI), ^{1}H NMR, and ^{13}C NMR for **WKC11**&**13** were provided in Supporting Information.

References

1. Mori, A.; Sugie, A. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 548.
https://doi.org/10.1246/bcsj.81.548
2. Schipper, D. J.; Fagnou, K. *Chem. Mater.* **2011**, *23*, 1594.
https://doi.org/10.1021/cm103483q
3. Burke, D. J.; Lipomi, D. J. *Energy Environ. Sci.* **2013**, *6*, 2053.
https://doi.org/10.1039/C3EE41096J
4. Okamoto, K.; Zhang, J.; Housekeeper, J. B.; Marder, S. R.; Luscombe, C. K. *Macromolecules* **2013**, *46*, 8059.
https://doi.org/10.1021/ma401190r
5. Mainville, M.; Leclerc, M. *ACS Appl. Polym. Mater.* **2021**, *3*, 2.
https://doi.org/10.1021/acsapm.0c00883
6. Liu, C. Y.; Lin, P. H.; Lee, K. M. *Chem. Rec.* **2021**, *21*, 3498.
https://doi.org/10.1002/tcr.202100101
7. Mori, A.; Sekiguchi, A.; Masui, K.; Shimada, T.; Horie, M.; Osakada, K.; Kawamoto, M.; Ikeda, T. *J. Am. Chem. Soc.* **2003**, *125,* 1700.
https://doi.org/10.1021/ja0289189
8. Masui, K.; Mori, A.; Okano, K.; Takamura, K.; Kinoshita, M.; Ikeda, T. *Org. Lett.* **2004**, *6*, 2011.
https://doi.org/10.1021/ol049386z
9. Shikuma, J.; Mori, A.; Masui, K.; Matsuura, R.; Sekiguchi, A.; Ikegami, H.; Kawamoto, M.; Ikeda, T. *Chem. Asian J.* **2007**, *2*, 301.
https://doi.org/10.1002/asia.200600305
10. Koumura, N.; Wang, Z. S.; Miyashita, M.; Uemura, Y.; Sekiguchi, H.; Cui, Y.; Mori, A.; Mori, S.; Hara, K. *J. Mater. Chem.* **2009**, *19*, 4829.
https://doi.org/10.1039/B905831A
11. Tamba, S.; Fujii, R.; Mori, A.; Hara, K.; Koumura, N. *Chem. Lett.* **2011**, *40*, 922.
https://doi.org/10.1246/cl.2011.922
12. Kawamata, Y.; Tokuji, S.; Yorimitsu, H.; Osuka, A. *Angew. Chem. Int. Ed.* **2011**, *50,* 8867.
https://doi.org/10.1002/anie.201102318
13. Mitamura, Y.; Yorimitsu, H.; Oshima, K.; Osuka, A. *Chem. Sci.* **2011**, *2,* 2017.
https://doi.org/10.1039/C1SC00372K
14. Yanagi, T.; Otsuka, S.; Kasuga, Y.; Fujimoto, K.; Murakami, K.; Nogi, K.; Yorimitsu, H.; Osuka, A. *J. Am. Chem. Soc.* **2016**, *138*, 14582.
https://doi.org/10.1021/jacs.6b10278
15. Shi, Y.; Yang, G.; Shen, B.; Yang, Y.; Yan, L.; Yang, F.; Liu, J.; Liao, X.; Yu, P.; Bin, Z.; You, J. *J. Am. Chem. Soc.* **2021**, *143*, 21066.
https://doi.org/10.1021/jacs.1c11277
16. Nitti, A.; Signorile, M.; Boiocchi, M.; Bianchi, G.; Po, R.; Pasini, D. *J. Org. Chem.* **2016**, *81*, 11035.
https://doi.org/10.1021/acs.joc.6b01922
17. Nitti, A.; Bianchi, G.; Po, R.; Swager, T. M.; Pasini, D. *J. Am. Chem. Soc.* **2017**, *139*, 8788.
https://doi.org/10.1021/jacs.7b03412
18. Nitti, A.; Osw, P.; Calcagno, G.; Botta, C.; Etkind, S. I.; Bianchi, G.; Po, R.; Swager, T. M.; Pasini, D. *Org. Lett.* **2020**, *22*, 3263.
https://doi.org/10.1021/acs.orglett.0c01043

19. Nitti, A.; Forti, G.; Bianchi, G.; Botta, C.; Tinti, F.; Gazzano, M.; Camaioni, N.; Po, R.; Pasini, D. *J. Mater. Chem. C.* **2021**, *9*, 9302.
    https://doi.org/10.1039/D1TC01887F
20. Corsini, F.; Nitti, A.; Tatsi, E.; Mattioli, G.; Botta, C.; Pasini, D.; Griffini, G. *Adv. Optical Mater.* **2021**, *9*, 2100182.
    https://doi.org/10.1002/adom.202100182
21. Lu, C.; Paramasivam, M.; Park, K.; Kim, C. H.; Kim, H. K. *ACS Appl. Mater. Interfaces*. **2019**, *11*, 14011.
    https://doi.org/10.1021/acsami.8b20646
22. Lin, P. H.; Lu, T. J.; Cai, D. J.; Lee, K. M.; Liu, C. Y. *ChemSusChem.* **2015**, *8,* 3222.
    https://doi.org/10.1002/cssc.201500993
23. Lu, T. J.; Lin, P. H.; Lee, K. M.; Liu, C. Y. *Eur. J. Org. Chem.* **2017**, 111.
    https://doi.org/10.1002/ejoc.201601257
24. Ciou, Y. S.; Lin, P. H.; Li, W. M.; Lee, K. M.; Liu, C. Y. *J. Org. Chem.* **2017**, *82*, 3538.
    https://doi.org/10.1021/acs.joc.7b00054
25. Huang, J. H.; Lin, P. H.; Li, W. M.; Lee, K. M.; Liu, C. Y. *ChemSusChem*. **2017**, *10,* 2284.
    https://doi.org/10.1002/cssc.201700421
26. Lu, K. M.; Li, W. M.; Lin, P. Y.; Liu, K. T.; Liu, C. Y. *Adv. Synth. Catal.* **2017**, *359,* 3805.
    https://doi.org/10.1002/adsc.201700762
27. Chang, Y. C.; Lee, K. M.; Lai, C. H.; Liu, C. Y. *Chem. Asian J.* **2018***, 13,* 1510.
    https://doi.org/10.1002/asia.201800454
28. Lu, K. M.; Lee, K. M.; Lai, C. H.; Ting, C. C.; Liu, C. Y. *Chem. Commun.* **2018***, 54,* 11495.
    https://doi.org/10.1039/C8CC06791K
29. Lin, P. H.; Lee, K. M.; Ting, C. C.; Liu, C. Y. *J. Mater. Chem. A.* **2019***, 7,* 5934.
    https://doi.org/10.1039/C8TA12274A
30. Chang, Y. C.; Lee, K. M.; Ting, C. C.; Liu, C. Y. *Mater. Chem. Front.* **2019***, 3,* 2041.
    https://doi.org/10.1039/C9QM00309F
31. Peng, Y. K.; Lee, K. M.; Ting, C. C.; Hsu, M. W.; Liu, C. Y. *J. Mater. Chem. A.* **2019**, *7*, 24765.
    https://doi.org/10.1039/C9TA09777E
32. Chen, J. H.; Lee, K. M.; Ting, C. C.; Liu, C. Y. *RSC Adv.* **2021**, *11*, 8879.
    https://doi.org/10.1039/D0RA10190G
33. Tu, C. H.; Lee, K. M.; Chen, J. H.; Chiang, C. H.; Hsu, S. C.; Hsu, M. W.; Liu, C. Y. *Org. Chem. Front.* **2022**, *9*, 2821.
    https://doi.org/10.1039/D2QO00187J