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Facile Synthetic Routes for Heteroatom-containing Alkylated/Arylated Polycyclic Aromatic Hydrocarbons

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Abstract: Simple synthetic routes for heteroatom-containing polycyclic aromatic hydrocarbons (H-PAHs) with alkyl and aryl substitution were demonstrated. Three H-PAHs including heteroatom containing rubicenes (H-rubicenes), angular-benzothiophenes (ABTs), and indenothiophene (IDTs) were successfully synthesized through two key steps including polysubstituted olefins formation and cyclization. Specifically, ABT and H-rubicenes were comprehensively investigated by single-crystal X-ray diffraction, NMR, UV-vis absorption, cyclic voltammetry, transient absorption and single crystal OFET measurements.

Heteroatom-containing polycyclic aromatic hydrocarbons (H-PAHs) have promising applications in organic electronics, such as organic light emitting diodes (OLEDs), organic solar cells (OSCs) and organic field effect transistors (OFETs) due to their unique chemical and physical properties.^[1] However, to pursue a simple, sustainable and economic synthetic pathway still remains a huge challenge, since many synthesis of H-PAHs usually require multi-steps syntheses and tedious purification processes.^[2] One important PAH, rubicene, is a fragment of C70, which demonstrated high charge transport mobilities and strong light absorption.^[3] Many synthetic efforts have been made to tune their electronic properties for opto-electronic applications.^[3b,4] Developing heteroatom-doped rubicenes is important to further modify their properties, while only nitrogen-doped rubicenes have been reported to date owing to the synthetic challenges pertaining

to ring strain and regioselectivity.^[4] For example, the early reports included ICl-mediated benzannulation of dialkyne, followed by cross coupling arylation, and finally Scholl oxidation (**Scheme 1a**).^[4d, 4e, 5] Another two typical H-PAHs, angular-benzothiophenes (ABTs) and indenothiophenes (IDTs) derivatives, were shown to exhibit excellent charge transport mobilities in electronic devices.^[6] In general, alkyl chains need to be introduced into the backbone of ABTs and IDTs for solution processability, which requires additional synthetic steps or harsh reaction conditions. For example, one synthetic method for alkylated ABTs requires borylation of an alkyne and subsequent Suzuki coupling reaction, resulting in overall low yields (**Scheme 1b**).^[6a] Also, synthesis of alkylated IDTs usually includes high energy consumption reactions, Wolff-Kishner reduction (**Scheme 1c**).^[6d, 7] Obviously, the complicated synthetic methods and overall low yield increased the cost of H-PAHs (**Scheme 1**), hindering their applications in organic electronics. Thus, it is important to develop facile and efficient routes to synthesize alkylated/arylated H-PAHs.

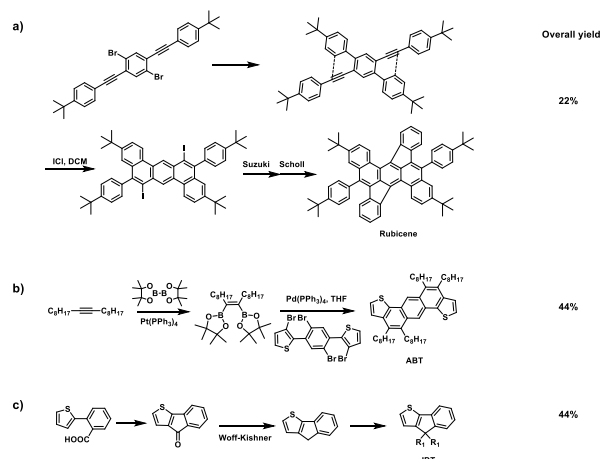
Disubstituted and trisubstituted olefins are important intermediates for organic synthesis,^[8] thus various methods were developed to synthesize these olefins.^[9] Recently, an efficient synthetic method for disubstituted or trisubstituted olefins via Pd-catalyzed cross coupling of N-tosylhydrazones and aryl halides were reported,^[10] which exhibited no need of stoichiometric organometallic reagents.^[11] Furthermore, most of N-tosylhydrazones are derived from commercially available ketones, which may provide a wide application scope for these olefins.^[10, 12] Therefore, to further explore the chemistry of these disubstituted or trisubstituted olefins is undoubtedly intriguing.^[8b, 12]

Herein three different kinds of H-PAHs (H-rubicenes (**4**), ABTs (**5**), and IDT (**6**)) with alkyl or arylated chains were successfully synthesized in two steps with remarkably overall yields upon three different cyclization of trisubstituted olefins (**3**). The structures of H-rubicene (**4a**, **4b** and **4d**) were confirmed by X-ray crystallography. Interestingly, the experimental results demonstrated that tuning the chalcogen atoms of H-rubicene (**4a** and **4b**) can significantly influence the intermolecular π - π stacking and thus charge transport mobilities, and the intersystem crossing (ISC) process, which were supported by OFETs, transient spectroscopy and electron paramagnetic resonance (EPR) spectroscopy.

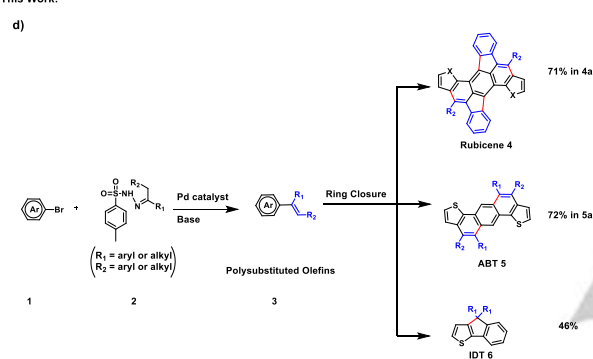
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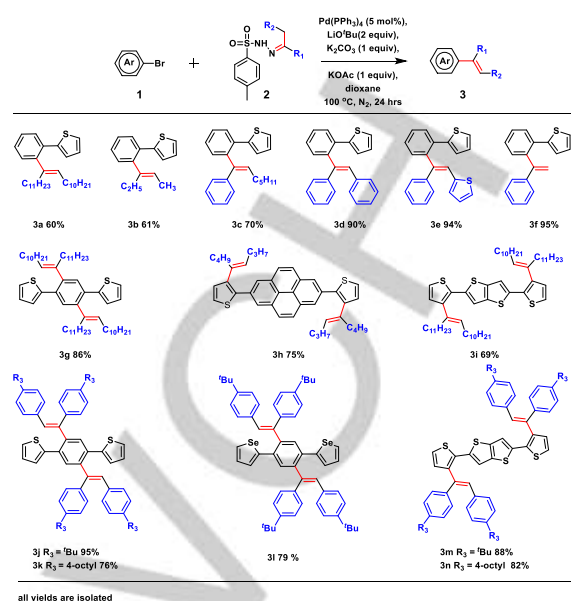
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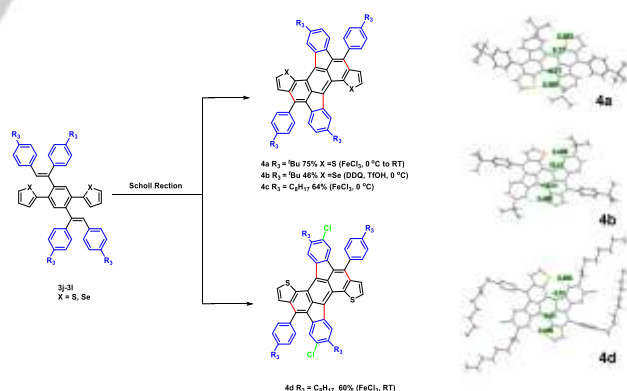
Scheme 1. Synthetic routes toward ABTs, IDTs and H-Rubicones.

Polysubstituted olefins with different alkyl or aryl chains (**3**) were synthesized via reaction of aromatic bromides with alkyl or aryl ketone N-tosylhydrazone (**Table 2**). The trial was initiated by the cross coupling between 2-(2-bromophenyl)-thiophene and 4-methyl-N'-(tricosan-12-ylidene)benzenesulfonohydrazone. Upon optimization of the base, a clean trisubstituted olefin **3a** was obtained in 60% yield (**Table S1**). Similar to previous reports, the reaction undergoes carbene migratory insertion.^[10-11] The variation of substituents R_1 and R_2 on N-tosylhydrazone (**2**) and modification of aryl units of aromatic bromides (**1**) open an avenue for building conjugated molecules for materials science. Therefore, various reactions of aromatic dibromides and ketone N-tosylhydrazone were performed to investigate the versatility of this method. In comparison to **3a**, **3b-3f** exhibited the successful modification of R_1 and R_2 , while **3g-3n** represented feasible variation on backbone through tuning aromatic dibromides. Overall, all trisubstituted and disubstituted olefins were synthesized with respectable yields (60%-95%), which suggested the excellent generality of this method.

Table 1. Substrates scope on aryl bromides and ketone N-tosylhydrazones.



To synthesize H-rubicones (**Scheme 3**), trisubstituted olefin **3j** was treated with FeCl_3 at 0 °C and then room temperature to afford **4a** in 75% yield, which is much more efficient than the reported methods.^[4b-d, 7] To the best of our knowledge, this is the first chalcogen-containing rubicene. Note that the overall yield of **4a** is above 60% in two steps, suggesting this new route is simple and efficient. To extend the reaction scope, **3k** with linear alkyl chain were oxidized with FeCl_3 at 0 °C to afford **4c**. When the temperature was increased to 25 °C, **3k** was converted to dichloride compound **4d** in a good yield of 60%, which may be directly used as a prefunctionality to synthesize rubicene-based small molecules and polymers. Moreover, **3l** was able to be converted to selenium-containing rubicene (**4b**) when DDQ was used as the oxidant reagent, which successfully realized the tuning of chalcogen atoms.

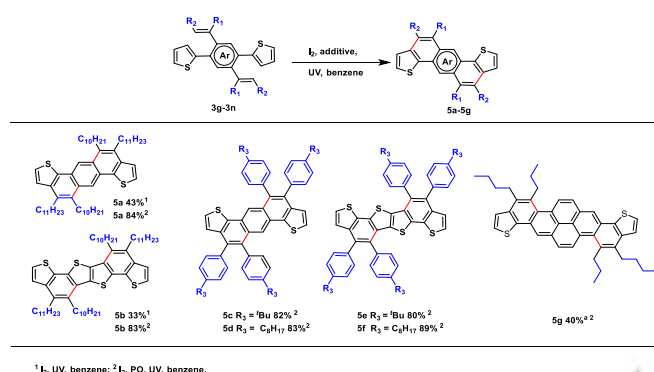


Scheme 3. Synthesis of H-rubicones via Scholl reaction and top view of crystal structures of H-rubicones.

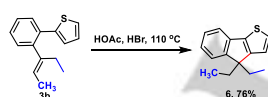
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Ladder type compounds ABTs were synthesized using dilolefins **3g-3n** (Table 2). Based on reported photocyclization conditions, ABT-derivatives (**5a** and **5b**) were synthesized with relatively low yields (30-50%).^[6b, 13] To optimize the photocyclization conditions, propylene oxide (PO) was added as an additive to afford much higher yields over 83% (**5b**), which may be ascribed to rapid elimination of HI side products.^[14] Under the optimal conditions, both alkyl and aryl olefins exhibited excellent reactivities, affording good yields of substituted ABTs (**5b-5g**). Significantly, the overall yield of **5b** is ca 57% including olefin formation and PO assisted photocyclization, which indicates this new route for ABTs is quite competitive.

Table 2. Photocyclization substrates scope.



In general, the formation of five-membered ring is more challenging than six-membered ring due to the higher ring strain of five-membered ring.^[15] The olefin **3b** was boiled under acid condition to afford 4,4-diethyl-4H-indeno[1,2-b]thiophene **6** with a yield of 76% (Scheme 4). This novel approach mostly relies on the selective protonation on the trisubstituted olefin, followed by electrophilic attack on an adjacent thiophene rings. The overall yield of 46% in two steps is significant in comparison to earlier reports.^[4]



Scheme 4. Cyclization based on Friedel-Crafts alkylation toward indenothiophene **6**.

All H-PAHs show excellent solubility on the common organic solvents, including hexanes, DCM, THF, etc. The structures of all H-PAHs were confirmed by 1H NMR, ^{13}C NMR, and mass spectra. Moreover, crystals of **4a**, **4b** and **4d** (Scheme 3) were grown by slow evaporation in chloroform for single crystal X-ray diffraction. As found from crystal structures, **4a** and **4b** adopted achiral antifolded backbones, while **4d** have a chiral twisted backbone in crystals (Figure S2). Notably, all H-rubicones possess slight twisted core with a torsion angle less than 10.4° , which are relatively smaller than all carbon based rubicones.^[3b, 6c] The smaller the torsion angles are, the shorter the chalcogen-hydrogen bond. Thus, the hydrogen bond may contribute to the

slightly more planar structure due to noncovalent through-space intramolecular interactions.^[16] Moreover, a interlayer distance (3.85 Å) was observed in crystals of **4a**, suggesting intermolecular $\pi-\pi$ interactions and excellent charge transport mobility (Figure S2).

To study chalcogen effect on electronic properties of rubicene for the first time, **4a** and **4b** were chosen as examples. The UV absorption spectra of **4a** and **4b** (Figure 1a) in chloroform exhibited two featured characteristic clusters of absorption peaks. In comparison to **4a**, an obvious red-shifts (13 nm) of the absorption peak was observed for **4b** solution, indicating Se atom increased quinoidal characteristics of the conjugated systems.^[17] Going from solution to film, small red-shifts (1-2 nm) of absorption peaks were observed for both **4a** and **4b**, suggesting both compounds possess weak $\pi-\pi$ intermolecular stacking. Cyclic voltammetry (Figure 1b) show both **4a** and **4b** have three quasi-reversible reductions and one irreversible oxidation. The onset oxidation and reduction potentials versus ferrocene are 0.69 and -0.96 V, 0.66 and -0.90 V for **4a** and **4b** (Table 3), respectively, which indicates **4b** is more easily to be oxidized and reduced than **4a**. From direct comparison of molecular packing and distance between central benzene plane of two neighboring molecules, **4a** exhibits a close and overlapping packing pattern between neighboring molecules, while **4b** molecules barely possess $\pi-\pi$ stacking. Meanwhile, two-dimensional (2D) ribbon single crystals (Figure 1c and 1d, inset) of **4a** and **4b** were prepared by physical vapor transport (PVT) on the 300 nm thermally grown SiO_2/Si substrates, which was supported by orthogonal polarized optical microscopy.^[18] No doubt that the devices based on the single crystals of **4a** exhibited a much higher hole transport mobility of $0.2\text{ cm}^2/V\cdot s$ with $I_{on/off}$ of 0.64×10^4 than **4b** ($0.0069\text{ cm}^2/V\cdot s$), which is among the highest values of rubicene type semiconductors.^[3b, 3c]

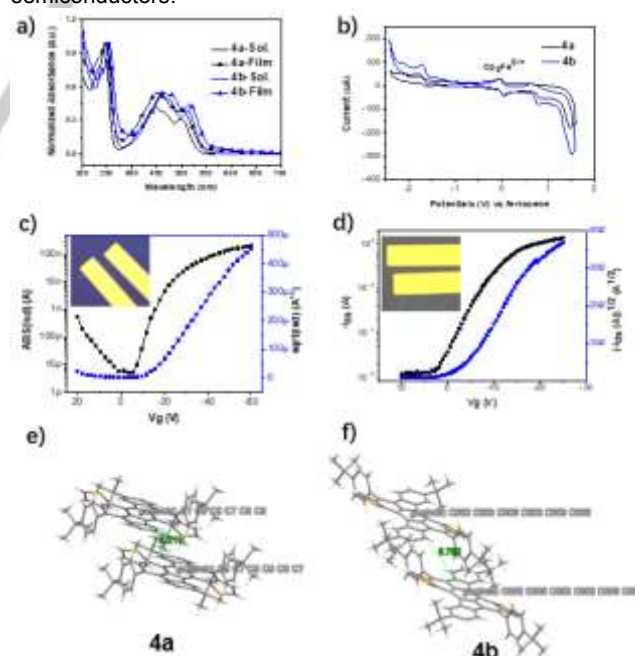


Figure 1. a) UV-vis absorption spectra of **4a** and **4b** in chloroform and in thin film. b) Cyclic voltammograms (CV) of **4a** and **4b** in $CH_2Cl_2/0.1\text{ M } [tBu_4N][PF_6]$ with ferrocenium/ferrocene as an internal standard. The horizontal scale refers

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to an Ag wire coated with AgCl as pseudo-reference electrode. **c**) and **d**) Transfer characteristics measured in the saturated regime of operation ($V_g = V_{sd} = -60$ V) for crystal **4a** and **4b**. Inset: optical microscopy image of devices. **e**) and **f**) molecular packing and centroid distance between crystals for **4a** and **4b**.

Table 3. Optical, electrochemical and charge transport properties.

Cmpd	λ_{sol}^a (nm)	λ_{fil}^a (nm)	E_{ox}^b (V)	E_{red}^b (V)	μ_h (cm ² /Vs)
4a	346, 446, 500	347, 450, 501	0.69	-0.96	0.2
4b	353, 459, 513	355, 462, 515	0.66	-0.90	0.0069

^aAbsorption maxima. ^b E_{ox} is the onset potential corresponding to oxidations, whereas E_{red} is the onset potential corresponding to reductions.

According to the golden rule of radiationless process, heavy atom effect and twist structure of **4b** may enhance the intersystem crossing (ISC) from the lowest singlet state (S_1) to the lowest triplet state (T_1). Thus, femtosecond transient absorption (TA) experiments were performed on **4a** and **4b** in toluene solution to investigate excited-state deactivation process upon photoexcitation. TA spectra for both **4a** and **4b** can be globally fitted with a sequential two-component model (Figure S17a and 18a). The former component (black line in Figure 2a and 2c) can be associated with the instantaneous populated S_1 , and the latter one (red line) is ascribed to long-lived T_1 state resulting from ISC process. A sharp difference between **4a** and **4b** is that the decaying rate of S_1 , whose lifetimes are 1.85 ns and 93.9 ps, respectively (Figure 2b and 2d). This clearly implies the ISC process is largely accelerated in the heavy-atom-containing **4b** compound. Therefore, **4b** exhibited a much higher triplet quantum yield than **4a** (~100% vs 38%), achieving the most efficient generation of triplet excitons through simple chalcogen atom tuning.^[19] The triplet nature of **4a** and **4b** were further confirmed by electron paramagnetic resonance (EPR) measurement (Figure S19) with strong EPR signals.

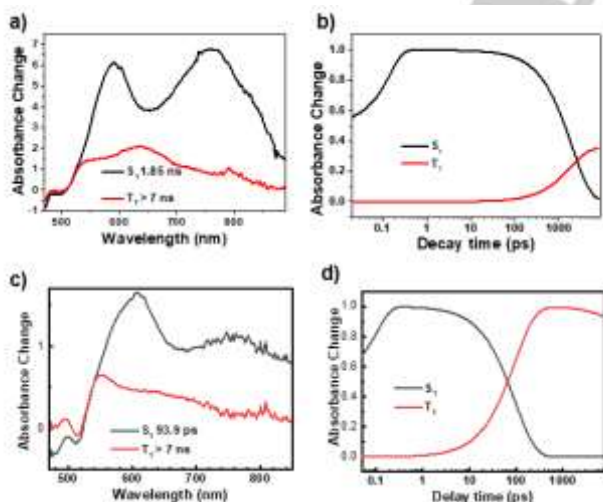


Figure 2. The species-associated difference spectra (SADS) and concentrations of transient species as a function of time obtained from global target analysis for **4a** (a, b) and **4b** (c, d).

The pyrene-containing ABT (**5g**) emitted deep blue light at around 462 nm in a fluorescent quantum yield of 9.4% in the solid (Figure S3). Additionally, the crystal OFET exhibited a good charge transport mobility of 0.02 cm²/Vs (Table S4). These

observations suggested ABT derivatives may be excellent materials for organic electronics.

In summary, simple and efficient synthetic routes for H-PAHs including H-rubicones, ABTs, and IDTs were developed with trisubstituted olefins as critical intermediates. These routes avoid toxic tin and flammable organolithium reagent or Grignard reagents. Additionally, ambient reaction conditions and inexpensive substrates make the synthetic routes cost-appealing. Significantly, a direct comparison between S- and Se-rubicone were investigated to show that chalcogen-atom doping greatly affected the physical properties such as crystal structures, energy levels, the charge transport mobilities and ISC efficiencies.

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- (a) X. Guo, M. Baumgarten, K. Müllen, *Prog. Polym. Sci.* **2013**, *38*, 1832-1908; (b) W. Jiang, Y. Li, Z. Wang, *Chem. Soc. Rev.* **2013**, *42*, 6113-6127; (c) A. P. Kulkarni, C. J. Tonzola, A. Babel, S. A. Jenekhe, *Chem. Mater.* **2004**, *16*, 4556-4573; (d) Y. Tao, C. Yang, J. Qin, *Chem. Soc. Rev.* **2011**, *40*, 2943-2970.
- (a) H. J. Bin, L. Gao, Z. G. Zhang, Y. K. Yang, Y. D. Zhang, C. F. Zhang, S. S. Chen, L. W. Xue, C. Yang, M. Xiao, Y. F. Li, *Nat. Commun.* **2016**, *7*; (b) Y. Z. Lin, Q. He, F. W. Zhao, L. J. Huo, J. Q. Mai, X. H. Lu, C. J. Su, T. F. Li, J. Y. Wang, J. S. Zhu, Y. M. Sun, C. R. Wang, X. W. Zhan, *J. Am. Chem. Soc.* **2016**, *138*, 2973-2976; (c) Y. Z. Lin, J. Y. Wang, Z. G. Zhang, H. T. Bai, Y. F. Li, D. B. Zhu, X. W. Zhan, *Adv. Mater.* **2015**, *27*, 1170-1174; (d) S. J. Xu, Z. C. Zhou, W. Y. Liu, Z. B. Zhang, F. Liu, H. P. Yan, X. Z. Zhu, *Adv. Mater.* **2017**, *29*.
- (a) H.-Y. Chen, J. Golder, S.-C. Yeh, C.-W. Lin, C.-T. Chen, C.-T. Chen, *RSC Adv.* **2015**, *5*, 3381-3385; (b) X. Gu, X. Xu, H. Li, Z. Liu, Q. Miao, *J. Am. Chem. Soc.* **2015**, *137*, 16203-16208; (c) H. Lee, Y. Zhang, L. Zhang, T. Mirabito, E. K. Burnett, S. Trahan, A. R. Mohebbi, S. C. B. Mannsfeld, F. Wudl, A. L. Briseno, *J. Mater. Chem. C* **2014**, *2*, 3361-3366.
- (a) O. Allemann, S. Duttwyler, P. Romanato, K. K. Baldrige, J. S. Siegel, *Science* **2011**, *332*, 574-577; (b) H. H. Hseuh, M. Y. Hsu, T. L. Wu, R. S. Liu, *J. Org. Chem.* **2009**, *74*, 8448-8451; (c) J. Liu, A. Narita, S. Osella, W. Zhang, D. Schollmeyer, D. Beljonne, X. Feng, K. Müllen, *J. Am. Chem. Soc.* **2016**, *138*, 2602-2608; (d) S. Toyota, M. Kawamura, E. Tsurumaki, *Synthesis* **2017**, *50*, 134-138.
- Y. S. Park, D. J. Dibble, J. Kim, R. C. Lopez, E. Vargas, A. A. Gorodetsky, *Angew. Chem. Int. Edit.* **2016**, *55*, 3352-3355.
- (a) L. Biniek, B. C. Schroeder, J. E. Donaghey, N. Yaacobi-Gross, R. S. Ashraf, Y. W. Soon, C. B. Nielsen, J. R. Durrant, T. D. Anthopoulos, I. McCulloch, *Macromolecules* **2013**, *46*, 727-735; (b) K. Hyodo, S. Nishinaga, Y. Sawanaka, T. Ishida, H. Mori, Y. Nishihara, *J. Org. Chem.* **2019**, *84*, 698-709; (c) J.-S. Wu, C.-T. Lin, C.-L. Wang, Y.-J. Cheng, C.-S. Hsu, *Chem. Mater.* **2012**, *24*, 2391-2399; (d) X. Li, F. Pan, C. Sun, M. Zhang, Z. Wang, J. Du, J. Wang,

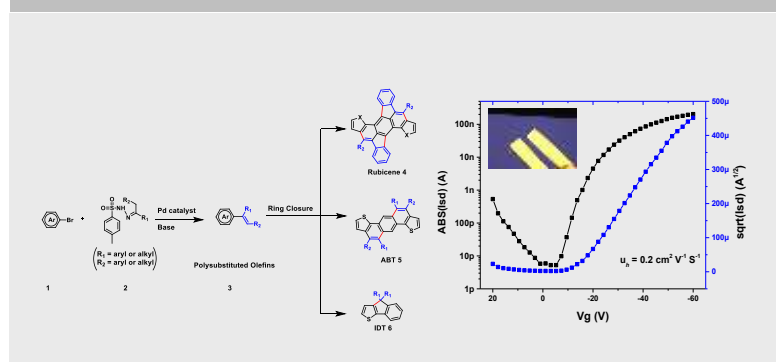
COMMUNICATION

- M. Xiao, L. Xue, Z. G. Zhang, C. Zhang, F. Liu, Y. Li, *Nat. Commun.* **2019**, *10*, 519; (e) L. Pouchain, O. Alévêque, Y. Nicolas, A. Oger, C.-H. Le Régent, M. Allain, P. Blanchard, J. Roncali, *J. Org. Chem.* **2009**, *74*, 1054-1064.
- [7] J. Bucevicius, P. Adomenasp, S. Tumkevicius, *Chem. Heterocycl. Com.* **2014**, *50*, 1413-1420.
- [8] (a) L. Zhou, F. Ye, J. Ma, Y. Zhang, J. Wang, *Angew. Chem. Int. Edit.* **2011**, *50*, 3510-3514; (b) K. Jiang, L. Zhang, Y. Zhao, J. Lin, M. Chen, *Macromolecules* **2018**, *51*, 9662-9668; (c) A. Pietrangelo, M. J. MacLachlan, M. O. Wolf, B. O. Patrick, *Org. Lett.* **2007**, *9*, 3571-3573.
- [9] Y. Xia, D. Qiu, J. Wang, *Chem. Rev.* **2017**, *117*, 13810-13889.
- [10] J. Barluenga, P. Moriel, C. Valdes, F. Aznar, *Angew. Chem. Int. Edit.* **2007**, *46*, 5587-5590.
- [11] (a) J. Barluenga, M. Escribano, F. Aznar, C. Valdés, *Angew. Chem. Int. Edit.* **2010**, *49*, 6856-6859; (b) K. L. Greenman, D. S. Carter, D. L. Van Vranken, *Tetrahedron* **2001**, *57*, 5219-5225.
- [12] C. Peng, Y. Wang, J. Wang, *J. Am. Chem. Soc.* **2008**, *130*, 1566-1567.
- [13] (a) M. B. Goldfinger, K. B. Crawford, T. M. Swager, *J. Am. Chem. Soc.* **1997**, *119*, 4578-4593; (b) A. Pietrangelo, B. O. Patrick, M. J. MacLachlan, M. O. Wolf, *J. Org. Chem.* **2009**, *74*, 4918-4926.
- [14] L. Liu, B. Yang, T. J. Katz, M. K. Poindexter, *J. Org. Chem.* **1991**, *56*, 3769-3775.
- [15] T. Dudev, C. Lim, *J. Am. Chem. Soc.* **1998**, *120*, 4450-4458.
- [16] H. Huang, L. Yang, A. Facchetti, T. J. Marks, *Chem. Rev.* **2017**, *117*, 10291-10318.
- [17] M. Planells, B. C. Schroeder, I. McCulloch, *Macromolecules* **2014**, *47*, 5889-5894.
- [18] Q. Tang, L. Jiang, Y. Tong, H. Li, Y. Liu, Z. Wang, W. Hu, Y. Liu, D. Zhu, *Adv. Mater.* **2008**, *20*, 2947-2951.
- [19] (a) T. Kobayashi, H. Kuramochi, T. Suzuki, T. Ichimura, *Phys. Chem. Chem. Phys.* **2010**, *12*, 5140-5148; (b) N. J. Turro, *Modern Molecular Photochemistry*, Benjamin Cummings, **1978**, pp. 98-100.

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Facile synthetic routes including trisubstituted olefins formation and cyclization were developed. Upon the optimization of reaction conditions, three different heteroatom-containing PAHs (H-rubicenes, ABTs, and IDTs) were successfully synthesized in relatively high overall yields. Finally, crystal structure, optoelectronic, radiationless process and charge transport properties of chalcogen containing rubicenes were investigated to show potentials in properties tuning and organic semiconductors.