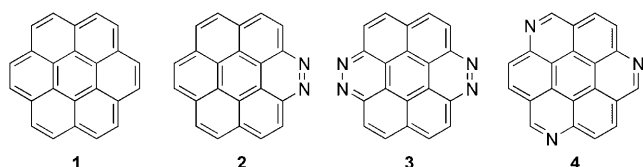


1,5,9-Triazacoronenes: A Family of Polycyclic Heteroarenes Synthesized by a Threefold Pictet–Spengler Reaction**

Junfa Wei,* Bo Han, Qiang Guo, Xianying Shi, Wenliang Wang, and Ni Wei

The design and synthesis of polycyclic aromatic hydrocarbons (PAHs) have been attracting considerable interest owing to their potential applications in organic optoelectronics, such as field-effect transistors, photovoltaic cells, and light-emitting diodes.^[1,2] One of the most commonly used methodologies for this purpose is the incorporation of heteroatoms into the aromatic framework of PAHs to improve their physicochemical properties and enhance the carrier transport of the system for applications as organic electronics.^[3] For example, the replacement of the CH groups with electronegative nitrogen atoms is able to facilitate the electron injection and transport properties of the materials.^[3a–f] Coronene (**1**) is a representative example of graphitic fragments with a zigzag periphery and just the right size for such processing techniques (Scheme 1).^[4–6] However, only a few reports describe routes

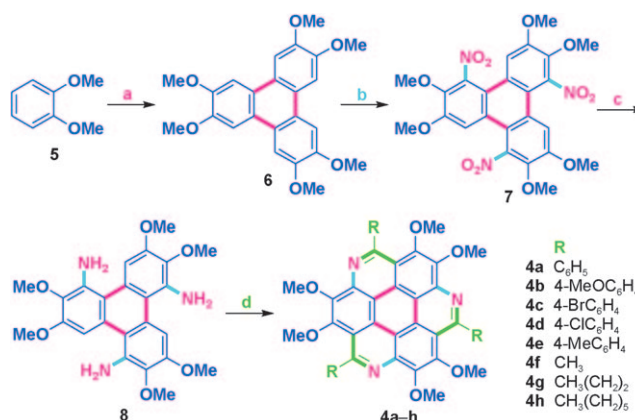


Scheme 1. Coronene and its polyaza derivatives.

to its nitrogenated analogues,^[7] such as 1,2-diazacoronene **2**^[7a] and 1,2,7,8-tetraazacoronene **3**,^[7b] which were obtained by the Diels–Alder reaction of perylene with diethyl azodicarboxylate and maleic anhydride at 350 °C. Obviously, the harsh preparative conditions and difficulties in selective modification have limited the further investigation of these azacoronenes.

We have designed and synthesized a new family of PAHs containing a 1,5,9-triazacoronene (TAC) core **4**, which can be regarded as a triple-fused isoquinoline or quinoline, from veratrole using a four-step sequence of trimerization, nitration, reduction, and a tandem threefold Pictet–Spengler reaction^[8] and oxidative aromatization under mild condi-

tions (Scheme 2). In addition to the preparative accessibility, these TAC derivatives have several advantages over their analogues, including: 1) the three electron-deficient pyridine



Scheme 2. The synthetic route to TACs: a) FeCl₃, CH₂Cl₂, 97%; b) fuming HNO₃, CH₂Cl₂, Et₂O, AcOH, reflux, 6 h, 28%; c) H₂, Raney Ni, EtOH, RT, 97%; d) RCHO, DMF, TFOH, 40–100 °C, 32–66%. DMF = *N,N*-dimethylformamide.

rings that should enhance the electron acceptor characteristics of the system; 2) three side-arms and six peripheral methoxy groups that should permit further functionalization to create new hetero-PAHs, starburst molecules, and dendrimers;^[9] and 3) three sets of 8-hydroxyquinoline and catechol moieties that should allow for further elaboration for constructing coordination supermolecules. Herein, we describe their synthesis, structure, and some of their essential properties.

Hexamethoxytriphenylene **6** was readily available through the trimerization of veratrole.^[10] Nitration of **6** with fuming nitric acid in a mixed solvent of acetic acid gave **7** as yellow needles in 28% yield. The next challenge was the reduction of **7** to the corresponding triamine **8**. Although many protocols have been well-established for reducing nitroarenes to arylamines, the catalytic hydrogenation over Raney nickel in ethanol was found to be the most favorable, giving triamine **8** in near-quantitative yield. The analytical and spectral data of intermediates **6–8** were perfectly self-consistent.

The key step was the triannulation of triamine **8** by inserting a methylidene group between the nitrogen atom and the adjacent benzene ring to build the isoquinoline motifs. A Pictet–Spengler reaction of **8** with benzaldehyde was chosen to furnish the triple ring-closure. After some investigation, we found that the triannulation and subsequent oxidative aro-

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matization reactions were achieved directly, thus providing **4a** in one-pot. The reaction was further improved to afford a 61% yield in *N,N*-dimethylformamide at 100°C in the presence of triflic acid. Analytical and spectral data match those expected from its C_3 -symmetrical geometry.

Encouraged by the success of such a one-pot triannulation of **8** with benzaldehyde, we used a range of aldehydes, both aromatic and aliphatic, to check the scope of our procedure, and, more importantly, to generate more TAC derivatives as candidate materials for the chemistry and materials communities (Table 1). The data revealed that both aromatic and aliphatic aldehydes afforded the desired products in promising yields.

Table 1: The triazacoronene derivatives synthesized by triannulation of the triamine **8** with various aldehydes.

| Entry | R | Yield [%] ^[a] | Entry | R | Yield [%] ^[a] |
|-----------|--|--------------------------|-----------|---|--------------------------|
| 4a | C ₆ H ₅ | 61 | 4e | 4-CH ₃ C ₆ H ₄ | 64 |
| 4b | 4-CH ₃ OC ₆ H ₄ | 66 | 4f | CH ₃ | 32 |
| 4c | 4-BrC ₆ H ₄ | 54 | 4g | CH ₃ CH ₂ CH ₂ | 51 |
| 4d | 4-ClC ₆ H ₄ | 53 | 4h | CH ₃ (CH ₂) ₄ CH ₂ | 50 |

[a] Conditions: triamine (0.55 mmol), aldehyde (3.3 mmol), *N,N*-dimethylformamide (2 mL), triflic acid (1%), 100°C (ArCHO) or 40°C (RCHO).

All of the TAC derivatives are soluble in common solvents, such as chloroform, tetrahydrofuran, dichloromethane, ethyl acetate, and acetone, giving yellowish-green-colored solutions with bright fluorescence. The good solubility (up to 25 mg mL⁻¹) permitted them to be processible in solution.

The characterization data of the products are consistent with their structures; the structure of **4b** was clearly confirmed by X-ray crystallography (Figure 1).^[11] Compound **4b** has a three-blade propeller-like shaped structure possessing the fundamental motif of coronene. The central benzene ring is a regular hexagon in which the six carbon atoms are

coplanar within 0.0066 Å, whilst both of the fused benzene and pyridine rings are slightly irregular. Interestingly, the side-view shows that the core is a slightly bowl-shaped structure wherein the fused rings bend out of the central ring plane by 4.15°, on average, to the same side to form a curve conformation. A likely reason is that the undersized N=C bonds (average length 1.342 Å) makes the perimeter too short to keep the core coplanar. In fact, the average bond length of the rim (1.393 Å) is shorter than that of the central ring (1.418 Å).

The six methoxy groups are oriented alternately above and below the core plane with dihedral angles near 90° for those adjacent to the nitrogen atoms and 60–70° for the rest. Each ring plane of the phenyl side-groups is twisted 69.9° (phenyl appended on C1), 70.5° (on C6), and 60.6° (on C11), respectively, from the pyridine moiety. Such orientations make it difficult for the peripheral groups to conjugate with the core in the solid state. In addition, the bowl-shaped core renders the molecule chiral with a rough C_3 symmetry in the crystal.

Table 2 summarizes the photophysical properties and thermal stabilities of five representative TACs, and Figure 2 shows the typical spectra of **4a** and **4g**. The strongest absorption peak of the aromatic derivatives appears at around 370 nm in the ultraviolet region of the spectrum, typical of a π - π^* transition, whilst the aliphatic analogues

Table 2: The photophysical properties, melting point, and temperature of thermal decomposition of the triazacoronene derivatives.

| Entry | λ_{\max} (Abs) [nm] ^[a] | λ_{\max} (Em) [nm] ^[a] | λ_{\max} (Ex) [nm] ^[a] | Stokes shifts | m.p. [°C] | T_d [°C] |
|-----------|--|---|---|---------------|-----------|------------|
| 4a | 278, 369 | 504 | 379 | 135 | > 300 | 331 |
| 4b | 277, 372 | 504 | 405 | 132 | 280–282 | 345 |
| 4c | 278, 372 | 508 | 406 | 136 | > 300 | 374 |
| 4g | 272, 351 | 471 | 362 | 120 | 149–151 | 316 |
| 4h | 272, 351 | 472 | 370 | 121 | 99–100 | 346 |

[a] 2.00×10^{-5} M in CHCl₃. Abs = absorbance, Em = emission, Ex = excitation.

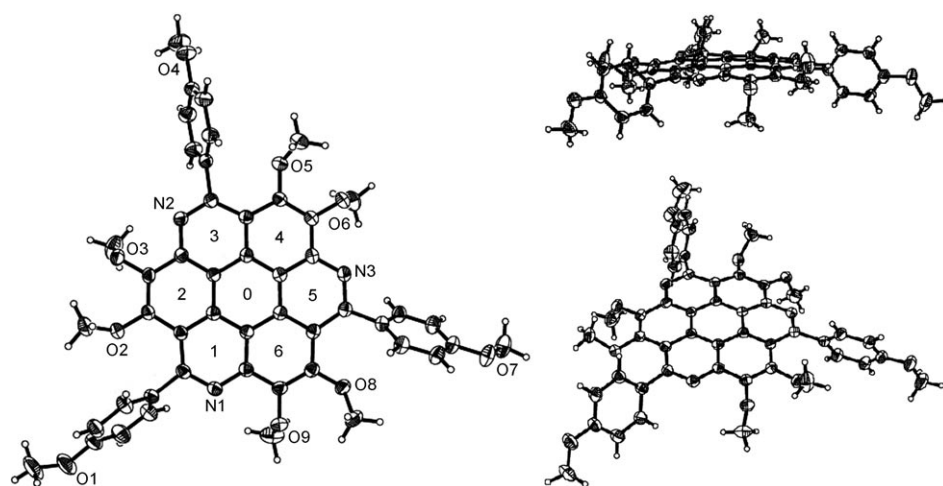


Figure 1. Molecular structure of **4b**: top view (left), side view (top right), and overall view (bottom right). Thermal ellipsoids set at the 30% probability level.

have an absorption maxima at 351 nm with a blue-shift of circa 20 nm relative to the aromatic analogues. This shift means that the side phenyl groups π -conjugate with the core to some extent. Compared with their all-carbon parent, 1,2,5,6,9,10-hexamethoxycoronene (HMC, 300 and 325 nm),^[6a] they are significantly red-shifted and have higher values for their molar extinction coefficient (4.1 – 10.4×10^5 M⁻¹ cm⁻¹). The remarkable differences between the TACs and HMC in their absorption peaks and intensities reflect the profound electronic effect of

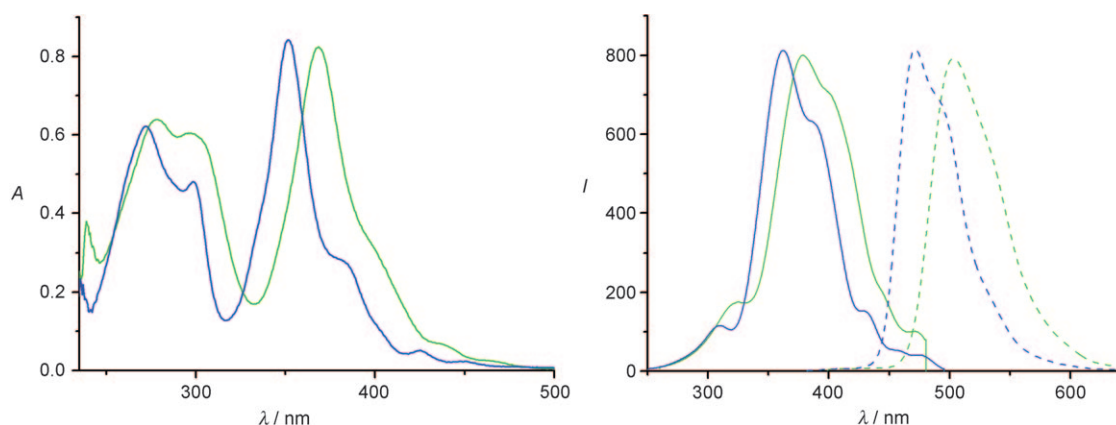


Figure 2. The electronic (left), emission, and excitation spectra (both right) of **4a** (green) and **4g** (blue) in CHCl_3 (2.00×10^{-5} M).

replacing the nitrogen atoms on the π -electron density of the system. The TACs show a strong blue-green emission under UV light and display large Stokes shifts ranging from 120 to 135 nm in their excitation spectra.

Cyclic voltammetry of the TACs (Table 3, Figure 3) revealed a reversible one-peak reduction with formal potentials (E°) of -1.58 to -1.91 V and irreversible oxidation waves of between 1.37 and 2.50 V vs Ag/AgCl, respectively.

Table 3: The electrochemical properties and energy levels of five representative compounds.

| Prod. | E_g (opt) [eV] ^[a] | E_{re} [V] ^[b] | E_{re} (onset) [V] | E_{ox1} [V] ^[b] | E_{ox1} (onset) [V] | E_{HOMO} [eV] ^[c] | E_{LUMO} [eV] ^[d] |
|--------------------|------------------------------------|--------------------------------|----------------------------|---------------------------------|-----------------------------|-----------------------------------|-----------------------------------|
| 4a | 2.67 | -1.59 | -1.30 | 1.47 | 1.36 | -6.07 | -3.41 |
| 4b | 2.64 | -1.58 | -1.45 | 1.43 | 1.34 | -6.05 | -3.26 |
| 4c | 2.62 | -1.91 | -1.74 | 1.55 | 1.26 | -6.06 | -3.45 |
| 4g | 2.75 | -1.68 | -1.61 | 1.48 | 1.28 | -5.99 | -3.10 |
| 4h | 2.76 | -1.77 | -1.62 | 1.37 | 1.29 | -6.00 | -3.09 |
| HMC ^[e] | 2.45 | -1.35 | | | | -5.5 | |

[a] Calculated from the λ_{max} values. [b] 0.1 M $[n\text{Bu}_4\text{N}][\text{ClO}_4]$ at a GC working electrode vs Ag/AgCl in CH_2Cl_2 . Scan rate 0.1 V s^{-1} . [c] $E_{HOMO} = -4.71 - E_{ox1}$ (onset). [d] $E_{LUMO} = -4.71 - E_{re}$ (onset). [e] See Ref. [6a].

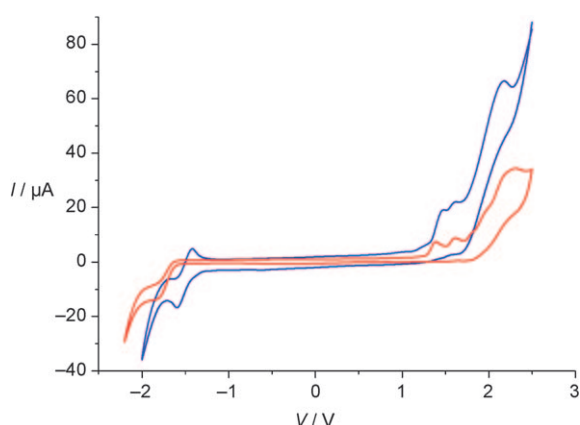


Figure 3. Cyclic voltammograms of **4a** (blue line) and **4h** (red line) in CH_2Cl_2 (2.00×10^{-3} M) containing 0.1 M $n\text{Bu}_4\text{NClO}_4$. Scan rate: 0.1 V s^{-1} .

The LUMO and HOMO energy levels were estimated at around -3.0 eV and -6.0 eV, based on the reduction and first oxidation onsets. Both energy levels are near to those of the commonly used hole-blocking materials, such as 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) and 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI),^[1k,12] and the HOMO levels are lower than those of HMC (-5.5 eV).^[6a] These results suggest that TACs constitute intrinsic n-type semiconducting materials with good hole-blocking and electron transport properties^[13] and agree with their π -deficient characterization owing to the electron-poor pyridine rings. The electrochemical energy gaps (E_g^{el}) were between 2.61–2.91 eV, near the optical gaps (E_g^{opt} , 2.62–2.76 eV).

All TACs produced strong electrogenerated chemiluminescence (ECL) emission for radical ion annihilation by stepping from the first oxidation wave ($E_{ox1} = +50$ mV) to the reduction wave ($E_{re} = -50$ mV; Table 3). Figure 4 shows the ECL for **4b** by stepping from 1.48 to -1.63 V, which can be seen with the naked eye in a dark room. As shown, highly stable and repeatable ECL emissions were observed under continuous stepping for 100 cycles. The operational stability is an important criteria when evaluating the performance of electroluminescent materials in terms of their practical

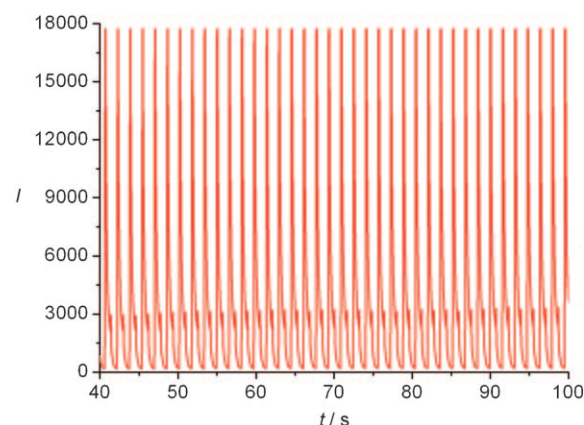


Figure 4. Stepping ECL (annihilation) of **4b** (2.00×10^{-3} M) in CH_2Cl_2 . Pulse width, 0.8 s; stepping direction is from the first oxidation peak to the reduction peak.

applications.^[14] A possible radical-ion annihilation can be proposed, in which TAC⁰ is oxidized to the radical cation TAC⁺ on the cathode and reduced to the radical anion TAC⁻ on the anode; the emission occurs in the annihilation of TAC⁻ and TAC⁺, wherein the singlet excited state of TAC* was formed.

Density functional theory (DFT) computations at the B3LYP/6-31G* level in a suite of Gaussian 03 programs showed that the optimized structure of the cores was in agreement with the X-ray crystal data (for the optimized structure, the electrostatic potentials, and the frontier molecular orbital energies, see the Supporting Information). The HOMOs in **4b** and **4g** were partially delocalized to the peripheral groups, whilst the LUMOs were mainly localized on the core (Figure 5). The calculated HOMO and LUMO

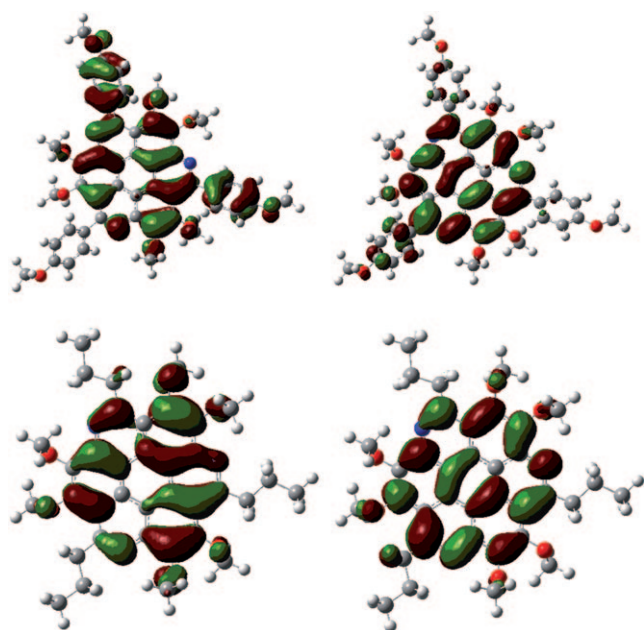


Figure 5. The orbital diagrams of **4b** (top) and **4g** (bottom): HOMO (left) and LUMO (right).

levels were systematically over-estimated in the DFT calculations. The HOMO–LUMO energy gaps E_g^s (2.82–3.02 eV) were uniformly higher than E_g^{opt} s and E_g^{el} s by approximately 0.2 eV. The discrepancies between the experimental and calculated values was presumably owing to the fact that the calculations were performed in a vacuum.^[15]

Thermogravimetric analysis revealed that the TACs were stable to above 300 °C, thus proving them to be thermally robust materials suitable for application in organic electronics.

In conclusion, a new family of triazacoronene derivatives has been designed and the first eight members have been synthesized from veratrole using a threefold Pictet–Spengler reaction as the key step. Their unique structure, admirable photophysical and electrical properties, good solubility, and high thermal stability should make this class of hetero-PAHs promising candidates for emissive and electron-transport materials. Moreover, the electron-deficient nature of the core

and the easily designable and modifiable groups on the periphery allow the TACs a new n-type center to create various star-shaped molecular networks, such as large heteroarenes, dendrimers, and supermolecules, or to tune their properties by installing desired subunits on the arms or extending the π -system. Synthetic efforts towards compounds of this type are currently underway.

Experimental Section

7: Fuming nitric acid (3.1 mL, 1.52 g cm⁻³) was added dropwise to a stirred suspension of 2,3,6,7,10,11-hexamethoxytriphenylene (3.00 g) in a mixture of AcOH, Et₂O, and CH₂Cl₂ (15.0 mL each). The mixture was stirred at reflux for 6 h and then the volatile solvents were removed under reduced pressure. The solution was poured into water and the resulting solid was filtrated, washed with water, and dried in vacuum. Column chromatography on silica gel (eluted with CHCl₃) and recrystallization from CHCl₃/EtOH gave **7** as yellow needles (1.11 g, 28% yield); m.p. 267–268 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.59 (s, 3H), 3.99 (s, 9H), 4.06 ppm (s, 9H); ¹³C NMR (75.45 MHz, CDCl₃): δ = 55.81, 62.09, 107.34, 114.05, 122.89, 141.64, 143.35, 152.03 ppm; elemental analysis calcd. (%) for C₂₄H₂₁N₃O₁₂: C 53.04, H 3.89, N 7.73; found: C 53.34, H 3.82, N 7.45.

8: A solution of **7** (0.50 g, 0.92 mmol) in EtOH (6.0 mL) was stirred with freshly prepared Raney nickel^[16] (1.07 g, 18.4 mmol) under a hydrogen atmosphere at room temperature and atmospheric pressure. After the absorption of hydrogen ceased, the catalyst was removed by filtration. The filtrate was evaporated to dryness in a vacuum and the residue was recrystallized from EtOH to give **8** as a grayish-white solid (0.40 g, 97% yield); m.p. 170–171 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.95 (s, 9H), 3.97 (s, 9H), 4.58 (s, 6H), 8.10 ppm (s, 3H); ¹³C NMR (75.45 MHz, CDCl₃): δ = 55.26, 59.73, 98.17, 113.68, 127.71, 134.39, 137.66, 150.04 ppm; elemental analysis calcd. (%) for C₂₄H₂₇N₃O₆: C 63.56, H 6.00, N 9.27; found: C 63.53, H 6.11, N 9.17.

General procedure for the synthesis of TACs (**4a–h**): A mixture of **8** (0.25 g, 0.55 mmol) and aldehyde (3.3 mmol) in DMF (2 mL) containing 1% triflic acid was stirred at 100 °C (40 °C for aliphatic aldehydes) until **8** could not be detected by TLC. Then the reaction mixture was diluted with water (10 mL), the solution was made basic with 15% aqueous NaOH solution, and extracted with CHCl₃ (20 mL). The organic phase was washed with brine (10 mL), dried with Na₂SO₄, and evaporated to dryness. The residue was purified by column chromatography on silica gel using hexane/ethyl acetate (1:8, v/v) as eluent to afford the product.

4b: (0.29 g, 66% yield), yellow solid, m.p. 275–277 °C; ¹H NMR (300 MHz, CDCl₃): δ = 7.16 (d, J = 6.9 Hz, 6H); 7.95 (d, J = 6.9 Hz, 6H); 4.57 (s, 9H); 3.99 (s, 9H); 3.78 ppm (s, 9H); ¹³C NMR (75.45 MHz, CDCl₃): δ = 159.8, 159.0, 150.2, 147.6, 139.8, 136.3, 131.5, 115.9, 112.8, 112.6, 63.1, 62.0, 55.5 ppm; elemental analysis calcd. (%) for C₄₈H₃₉N₃O₉: C 71.90, H 4.90, N 5.24; found: C 71.77, H 4.95, N 5.29.

4g: (0.17 g, 51% yield), yellow solid, mp 146–147 °C. ¹H NMR (300 MHz, CDCl₃): δ = 4.54 (s, 9H), 4.47 (s, 9H), 4.12 (d, 6H), 2.26 (t, 6H), 1.27 ppm (t, 9H); ¹³C NMR (75.45 MHz, CDCl₃): δ = 162.8, 150.7, 146.9, 139.5, 123.3, 116.3, 112.4, 62.7, 62.3, 42.8, 29.7, 23.8, 14.7 ppm; elemental analysis calcd. (%) for C₃₆H₃₉N₃O₆: C 70.92, H 6.45, N 6.89; found: C 70.75, H 6.48, N 6.96.

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- [1] For recent reviews, see: a) S. Allard, M. Forster, B. Souharce, H. Thiem, U. Scherf, *Angew. Chem.* **2008**, *120*, 4138–4167; *Angew. Chem. Int. Ed.* **2008**, *47*, 4070–4098; b) S. Günes, H. Neugebauer, N. S. Sariciftci, *Chem. Rev.* **2007**, *107*, 1324–1338; c) W. Pisula, A. K. Mishra, J. Li, M. Baumgarten, K. Müllen, *Org. Photovoltaics* **2008**, 93–128; d) B. C. Thompson, J. M. J. Frechet, *Angew. Chem.* **2008**, *120*, 62–82; *Angew. Chem. Int. Ed.* **2008**, *47*, 58–77; e) J. E. Anthony, *Angew. Chem.* **2008**, *120*, 460–492; *Angew. Chem. Int. Ed.* **2008**, *47*, 452–483; f) Y. Shirota, H. Kageyama, *Chem. Rev.* **2007**, *107*, 953–1010; g) A. C. Arias, J. D. MacKenzie, I. McCulloch, J. Rivnay, A. Salleo, *Chem. Rev.* **2010**, *110*, 3–24; h) X. Meng, W. Zhu, H. Tian, *Opt. Sci. Eng.* **2008**, *133*, 129–172; i) A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes, *Chem. Rev.* **2009**, *109*, 897–1091; j) M. Mas-Torrent, C. Rovira, *Chem. Soc. Rev.* **2008**, *37*, 827–838; k) A. P. Kulkarni, C. J. Tonzola, A. Babel, S. A. Jenekhe, *Chem. Mater.* **2004**, *16*, 4556–4573.
- [2] For examples, see: a) T. Yamamoto, T. Fukushima, A. Kosaka, W. Jin, Y. Yamamoto, N. Ishii, T. Aida, *Angew. Chem.* **2008**, *120*, 1696–1699; *Angew. Chem. Int. Ed.* **2008**, *47*, 1672–1675; b) Y. Fogel, M. Kastler, Z. Wang, D. Andrienko, G. J. Bodwell, K. Müllen, *J. Am. Chem. Soc.* **2007**, *129*, 11743–11749; c) J.-L. Wang, Y. Zhou, Y. Li, J. Pei, *J. Org. Chem.* **2009**, *74*, 7449–7456; d) J.-L. Wang, J. Yan, Z.-M. Tang, Q. Xiao, Y. Ma, J. Pei, *J. Am. Chem. Soc.* **2008**, *130*, 9952–9962; e) B. Ma, C. H. Woo, Y. Miyamoto, J. M. J. Frechet, *Chem. Mater.* **2009**, *21*, 1413–1417.
- [3] a) M. Takase, V. Enkelmann, D. Sebastiani, M. Baumgarten, K. Müllen, *Angew. Chem.* **2007**, *119*, 5620–5623; *Angew. Chem. Int. Ed.* **2007**, *46*, 5524–5527; b) D. Wu, W. Pisula, M. C. Haberecht, X. Feng, K. Müllen, *Org. Lett.* **2009**, *11*, 5686–5689; c) S. Barlow, Q. Zhang, B. R. Kafarani, C. Risko, F. Amy, C. K. Chan, B. Domercq, Z. A. Starikova, M. Y. Antipin, T. V. Timofeeva, B. Kippelen, J. L. Bredas, A. Kahn, S. R. Marder, *Chem. Eur. J.* **2007**, *13*, 3537–3547; d) M. J. D. Bosdet, W. E. Piers, T. S. Sorensen, M. Parvez, *Angew. Chem.* **2007**, *119*, 5028–5031; *Angew. Chem. Int. Ed.* **2007**, *46*, 4940–4943; e) S. Alibert-Fouet, I. Seguy, J. F. Bobo, P. Destruel, H. Bock, *Chem. Eur. J.* **2007**, *13*, 1746–1753; f) W. Jiang, Y. Li, W. Yue, Y. Zhen, J. Qu, Z. Wang, *Org. Lett.* **2010**, *12*, 228–231; g) Y. Sun, L. Tan, S. Jiang, H. Qian, Z. Wang, *J. Am. Chem. Soc.* **2007**, *129*, 1882–1883; h) J.-F. Wei, X.-W. Jia, J. Yu, X.-Y. Shi, C.-J. Zhang, Z.-G. Chen, *Chem. Commun.* **2009**, 4714–4716.
- [4] A. Léger, L. Hendecourt in *Polycyclic Aromatic Hydrocarbons and Astrophysics* (Eds.: A. Léger, et al.), Reidel, Dordrecht, The Netherlands, **1987**, p. 223.
- [5] a) A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**, *6*, 183–191; b) K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, *306*, 666–669; c) J. M. Schulman, R. L. Disch, *J. Phys. Chem. A* **1997**, *101*, 9176–9179; d) M. D. Watson, M. G. Debije, J. M. Warman, K. Müllen, *J. Am. Chem. Soc.* **2004**, *126*, 766–771; e) B. K. Spraul, S. Suresh, S. Glaser, D. Perahia, J. Ballato, D. W. Smith, Jr., *J. Am. Chem. Soc.* **2004**, *126*, 12772–12773; f) V. Palermo, S. Morelli, C. Simpson, K. Müllen, P. Samori, *J. Mater. Chem.* **2006**, *16*, 266–271; g) H. C. Shen, J. M. Tang, H. K. Chang, C. W. Yang, R. S. Liu, *J. Org. Chem.* **2005**, *70*, 10113–10116; h) W. W. H. Wong, D. J. Jones, C. Yan, S. E. Watkins, S. King, S. A. Haque, X. Wen, K. P. Ghiggino, A. B. Holmes, *Org. Lett.* **2009**, *11*, 975–978.
- [6] a) R. Rieger, M. Kastler, V. Enkelmann, K. Müllen, *Chem. Eur. J.* **2008**, *14*, 6322–6325; b) S. Xiao, J. Tang, T. Beetz, X. Guo, N. Tremblay, T. Siegrist, Y. Zhu, M. Steigerwald, C. Nuckolls, *J. Am. Chem. Soc.* **2006**, *128*, 10700–10701; c) A. M. van de Craats, J. M. Warman, A. Fechtenkötter, J. D. Brand, M. A. Harbison, K. Müllen, *Adv. Mater.* **1999**, *11*, 1469–1472; d) H.-P. Jia, S.-X. Liu, L. Sanguinet, E. Levillain, S. Decurtins, *J. Org. Chem.* **2009**, *74*, 5727–5729; e) J. L. Mynar, T. Yamamoto, A. Kosaka, T. Fukushima, N. Ishii, T. Aida, *J. Am. Chem. Soc.* **2008**, *130*, 1530–1531.
- [7] a) S. Tokita, K. Hiruta, K. Kitahara, H. Nishi, *Synth. Comm.* **1982**, 229–231; b) S. Tokita, K. Hiruta, K. Kitahara, H. Nishi, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3933–3934.
- [8] For Pictet–Spengler condensations, see: a) E. D. Cox, J. M. Cook, *Chem. Rev.* **1995**, *95*, 1797–1842; b) J. Royer, M. Bonin, L. Micouin, *Chem. Rev.* **2004**, *104*, 2311–2352.
- [9] G. R. Newkome, C. D. Shreiner, *Polymer* **2008**, *49*, 1–173.
- [10] N. Boden, R. C. Borner, R. J. Bushby, A. N. Cammidge, M. V. Jesudason, *Liq. Cryst.* **1993**, *15*, 851–858.
- [11] CCDC 788011 (**4b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Crystal data for **4b**: single crystals suitable for X-ray diffraction were obtained by slowly evaporating a solution of **4b** in tetrahydrofuran over one week. C₄₈H₃₉N₃O₉·2.5(C₄H₈O), *M* = 982.08, Triclinic, space group *P* $\bar{1}$, *a* = 11.993(4) Å, *b* = 13.599(4) Å, *c* = 18.240(6) Å, α = 111.631(4)°, β = 107.684(4)°, γ = 90.120(4)°, *V* = 2612.8(14) Å³, *T* = 296(2) K, *Z* = 2, $\mu(\text{Mo}_{\text{K}\alpha})$ = 0.71073 Å⁻¹, colorless square-plates, crystal dimensions 0.40 × 0.25 × 0.19 mm, crystal density 1.248 Mg m⁻³. Full matrix least-squares based on *F*², gave *R*₁ = 0.0779 and ωR_2 = 0.2410 for 9092 (*I* ≥ 2σ(*I*)), GOF = 1.033 for 686 parameters.
- [12] a) M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, P. E. Forrest, *Appl. Phys. Lett.* **1999**, *75*, 4–6; b) H. Xin, F. Y. Li, M. Shi, Z. Q. Bian, C. H. Huang, *J. Am. Chem. Soc.* **2003**, *125*, 7166–7167.
- [13] a) H.-B. Bürgi, K. K. Baldrige, K. Hardcastle, N. L. Frank, P. Gantzel, J. S. Siegel, J. Ziller, *Angew. Chem.* **1995**, *107*, 1575–1577; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1454–1456; b) C. R. Newman, C. D. Frisbie, D. A. da Silva Filho, J. L. Bredas, P. C. Ewbank, K. R. Mann, *Chem. Mater.* **2004**, *16*, 4436–4451.
- [14] a) J. I. Kim, I. S. Shin, H. Kim, J. K. Lee, *J. Am. Chem. Soc.* **2005**, *127*, 1614–1615; b) X. Liu, L. Shi, W. Niu, H. Li, G. Xu, *Angew. Chem.* **2007**, *119*, 425–428; *Angew. Chem. Int. Ed.* **2007**, *46*, 421–424; c) C. Booker, X. Wang, S. Haroun, J. Zhou, M. Jennings, B. L. Pagenkopf, Z. Ding, *Angew. Chem.* **2008**, *120*, 7845–7849; *Angew. Chem. Int. Ed.* **2008**, *47*, 7731–7735; d) K. M. Omer, S.-Y. Ku, K.-T. Wong, A. J. Bard, *J. Am. Chem. Soc.* **2009**, *131*, 10733–10741.
- [15] a) C.-G. Zhan, J. A. Nichols, D. A. Dixon, *J. Phys. Chem. A* **2003**, *107*, 4184–4195; b) V. Lukeš, R. Šolc, H. Lischka, H. F. Kauffmann, *J. Phys. Chem. A* **2009**, *113*, 14141–14149; c) C. Pérez-Bolívar, V. A. Montes, P. Anzenbacher, Jr., *Inorg. Chem.* **2006**, *45*, 9610–9612.
- [16] L. W. Convert, H. Adkins, *J. Am. Chem. Soc.* **1932**, *54*, 4116–4117.