

A Concise Method for Synthesizing 1,4,8,11-Tetraaza-6,13-dioxapentacene Derivatives

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Abstract: A concise method for preparing five tetraazadioxaacene derivatives through condensation reactions between 2,3,7,8-tetraaminodibenzo-1,4-dioxin tetrahydrochloride and commercially available diketones has been developed. The as-prepared compounds have interesting photophysical and electrochemical properties. Cyclic voltammetry measurements demonstrate that compounds **4** and **5** have less negative reduction potentials, which is inconsistent with the results of DFT calculations, and both might be promising for use as active elements in organic electronics.

Keywords: density functional calculations • diketones • dioxatetraazapentacenes • oligoacenes • organic electronics

Introduction

Oligoacenes have been receiving considerable interest because of their promising electronic properties and potential applications in electronic and optoelectronic devices, including organic field-effect transistors, photovoltaic cells, and light-emitting diodes (OLEDs).^[1–3] As the charge-transport nature of oligoacenes is *p*-type and switching their properties from *p*-type to *n*-type through the substitution of the hydrogen atoms with electron-withdrawing groups is tedious, an attractive method to realize this switching is the introduction of electronegative elements, for example nitrogen atoms, into the backbone of oligoacenes.^[4–7] In the last few decades, N-substituted heteroacenes have been frequently studied and several compounds have demonstrated some reasonable electron mobility.^[4,5] To further tune the properties of heteroacenes, inserting two or more different

types of heteroatoms into the frameworks of oligoacenes would offer scientists more opportunities because the properties of heteroacenes strongly depend on the type, position, number, and ratio of different heteroatoms.^[8]

In our previous research, we have reported several N-substituted heteroacenes and found that they have potential applications in OLEDs and ion sensing.^[7] Continuing our research in this direction, we are more interested in tetraazadioxaacene derivatives (Figure 1) because the synthe-

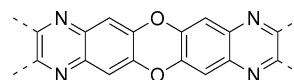


Figure 1. Molecular motif of tetraazadioxaacenes compounds.

sis should be more of a challenge, more novel properties could be achieved through carefully selecting the heteroatoms in backbone and tuning their positions, and heteroacenes could be more stable compared with their parent compounds. But until now, only a few dioxaaacene derivatives of dioxadiazacenes^[9] and triphenodioxazine^[10] have been reported and tetraazadioxaacenes are rare.

Herein, we report a concise way to prepare five new *n*-type tetraazadioxaacenes derivatives (Scheme 1): 2,3,9,10-tetramethyl-1,4,8,11-tetraaza-6,13-dioxapentacene (**MAOP**, **1**), 2,3,9,10-tetraethyl-1,4,8,11-tetraaza-6,13-dioxapentacene (**EAOP**, **2**), 2,3,9,10-tetraphenyl-1,4,8,11-tetraaza-6,13-dioxapentacene (**PAOP**, **3**), 9,12,21,24-tetraaza-10,23-dioxabenzof[a, c, p, r]heptacene (**TAOH**, **4**) and 4,5,9,12,21,24-hexaaza-10,23-dioxabenzof[a, c, p, r]heptacene (**HAOH**, **5**).

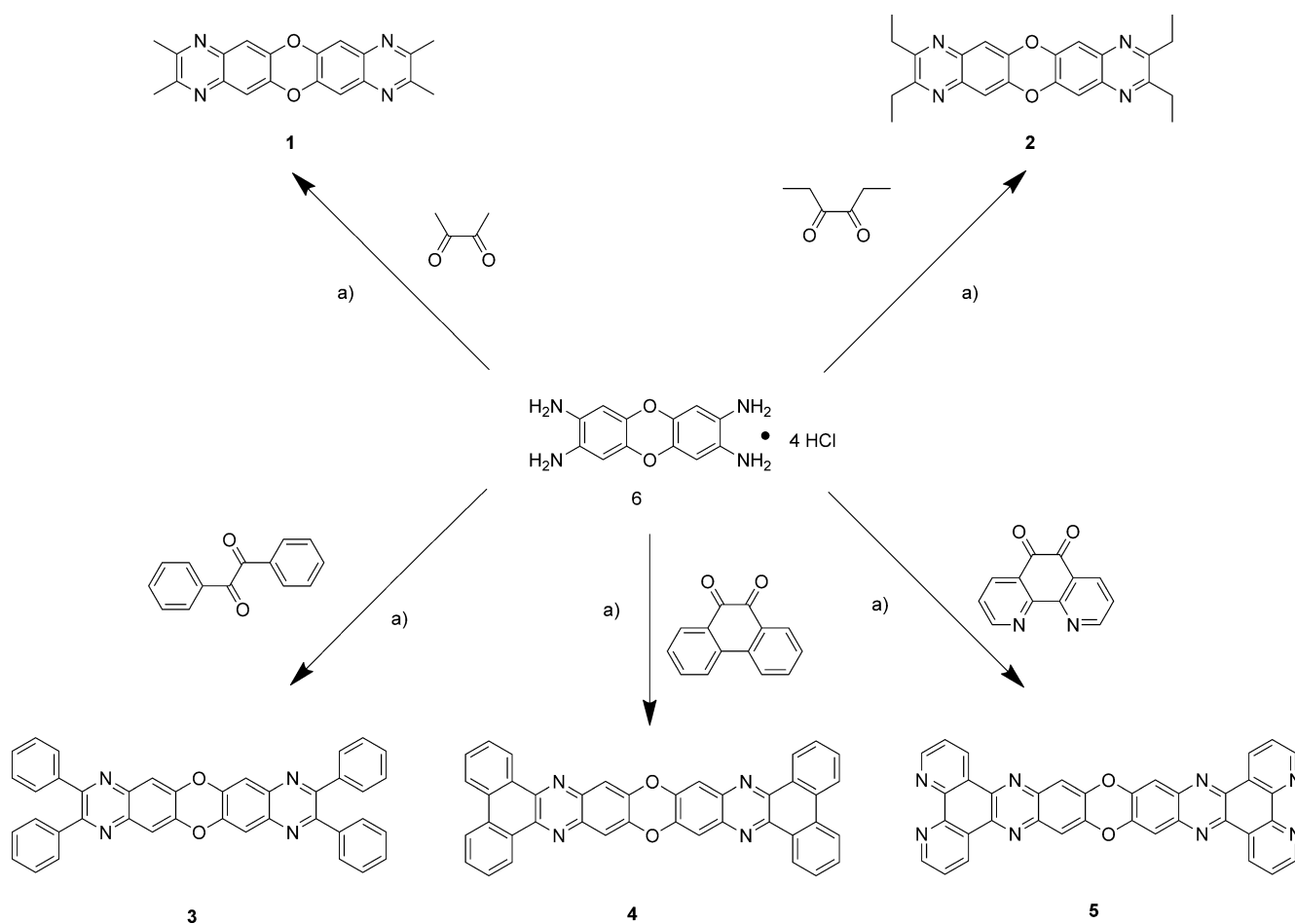
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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ajoc.201300095>.



Scheme 1. The synthetic routes to **1–5**. Reaction conditions: a) acetic acid, IBX, reflux, 48 h.

Results and Discussion

As shown in Scheme 1, tetraazadioxapentacene derivatives **1–5** were successfully synthesized through the cyclocondensation reaction between 2,3,7,8-tetraaminodibenzo-1,4-dioxin tetrahydrochloride (**6**) and the corresponding commercially available diketones in acetic acid in the presence of 2-iodoxybenzoic acid (IBX, Scheme 1). All as-prepared compounds were fully characterized by ^1H and ^{13}C NMR spectroscopy, FT-IR, and high-resolution mass spectrometry (see the Supporting Information).

The electronic absorption spectra of the five heteroacenes and the corresponding photophysical data are presented in Figure 2 and Table 1, respectively. The absorption spectra of compounds **1–5** (Figure 2a) have maximum bands at 381, 368, 397, 437, and 440 nm, respectively, which can be assigned to intramolecular charge transfer from the electron-donating unit to the electron-withdrawing group.

In trifluoroacetic acid solution (Figure 2b), the UV/vis absorptions of all compounds were bathochromically shifted compared with those in *N,N*-dimethylformamide (DMF) solution. The fluorescence spectra of all of the compounds in DMF solutions are shown in Figure S26 in the Supporting Information. Only compounds **2** and **3** gave relatively

Table 1. Summary of absorption and electrochemical properties of **1–5**.

Comp.	Absorption λ_{max} [nm]	$E_{\text{red}}^{1/2}$ [V] ^[a]	LUMO [eV] ^[b]	HOMO [eV] ^[c]	E_{gap} [eV] ^[d]
1	381	−1.90	−2.50	−5.75	3.25
2	368	−1.90	−2.50	−5.87	3.37
3	397	−1.91	−2.49	−5.61	3.12
4	437	−1.81	−2.59	−5.42	2.83
5	440	−1.78	−2.62	−5.43	2.81

[a] Obtained from cyclic voltammograms in heated DMF. Reference electrode: Ag/AgCl. [b] Calculated from cyclic voltammograms. [c] Calculated according to the formula $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{gap}}$. [d] Optical band gap, $E_{\text{gap}} = 1240/\lambda_{\text{max}}$.

strong fluorescence with maximum peaks at 387 nm and 417 nm, respectively.

To understand the molecular orbital energy levels, cyclic voltammetry (CV) measurements were carried out in degassed, anhydrous DMF solution (0.1 M $(n\text{Bu})_4\text{NPF}_6$, 80 °C) with Ag/AgCl as a reference electrode (Figure 3 and Table 1). The redox behavior of the five compounds is similar, with one reversible reduction couple in the negative region. The half-wave reduction potentials for compounds **1–5** are in the range −1.90–−1.78 V, which corresponds to LUMO energy levels of between −2.50–−2.62 eV when cal-

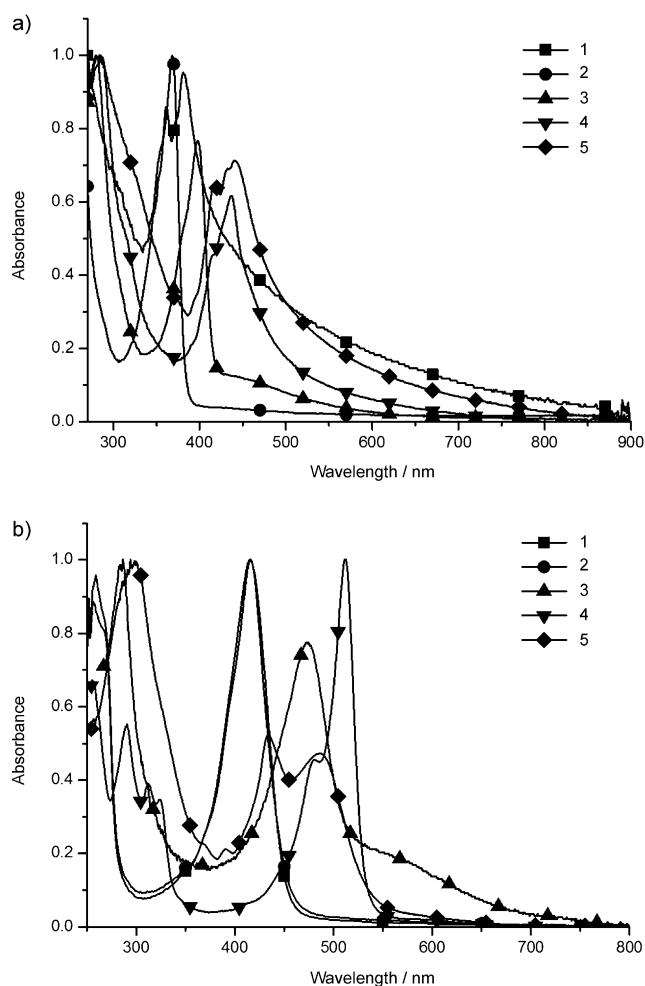


Figure 2. UV/vis spectra of **1–5** in a) DMF solutions and b) TFA solutions. Concentration = 5×10^{-5} M.

culated from the equation $E_{\text{LUMO}} = -e(4.40 + E_{\text{red}}^{1/2})$ eV.^[11] The reduction potentials of compounds **4** and **5** are shifted toward less negative potentials because the conjugation is extended relative to compounds **1**, **2**, and **3**. The bandgaps of the five conjugated heterocyclic compounds were estimated from the maximum absorption wavelength, which is in the range -2.81 – -3.37 eV. Similarly, the HOMO energy level, estimated from the formula $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{gap}}$, fell within the range -5.87 – -5.42 eV. Two different fused aromatic groups substituted at the periphery, anthracene and

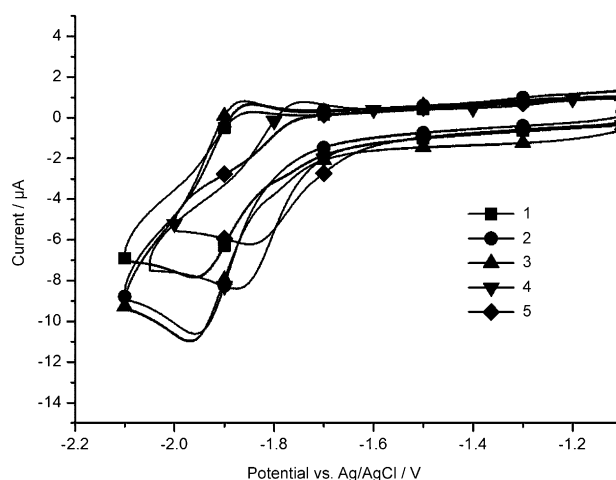


Figure 3. Cyclic voltammograms of **1–5**.

morpholine have a significant effect on the HOMO levels and these compounds have higher energy levels.

To gain more insight into the electronic and optical properties of these heteroacene derivatives, their optimized geometry was calculated by using DFT (B3LYP/6-31G*),^[12,13] and subsequent frequency analysis assured that the optimized structures were stable states. Time-dependent DFT (TDDFT) calculation of the $S_0 \rightarrow S_n$ transitions, using the same functional and basis set, were then performed based on the optimized structures in the ground states in combination with an integral equation formalism-polarizable continuum model (IEF-PCM, in DMF). Typically, the lowest 30 singlet roots of the nonhermitian eigenvalue equations were obtained to determine the vertical excitation energies. Oscillator strengths were deduced from the dipole transition matrix elements for singlet states only. All calculations were carried out with Gaussian 09.^[14] The simulated UV/vis absorbance bands and spectra, shown in Table 2 and Figure S27–S31 in the Supporting Information, gave computed λ_{max} values of 369.32, 366.4, 416.28, 449.68, and 441.48 nm, which are close to the experimental results. This absorption mainly corresponds to a pure HOMO–LUMO transition ($>96\%$) with π – π^* character.

The HOMO and LUMO orbitals of compounds **1–5** are all delocalized on the hexazapentacene backbones (shown in the Supporting Information, Figure S32–S46). Not only are the HOMO and LUMO orbitals of **3** delocalized on the hexazapentacene framework, but the phenyl groups also

Table 2. Computed absorption wavelength with corresponding oscillator strength, energy levels, and band gaps.

	S0–S1 [nm]	f	Assignments	Composition [%]	HOMO [eV]	LUMO [eV]	Gap [eV]
1	369.32	1.0451	HOMO → LUMO	97.65	–5.75	–1.80	3.95
2	366.4	1.0666	HOMO → LUMO	97.57	–5.70	–1.73	3.97
3	416.28	1.5937	HOMO → LUMO HOMO-2 → LUMO+1	96.11 2.77	–5.66	–2.09	3.58
4	449.68	1.8399	HOMO → LUMO HOMO-3 → LUMO+1	96.99 2.21	–5.72	–2.39	3.33
5	441.48	1.7974	HOMO → LUMO	97.77	–6.08	–2.69	3.39

participate in the orbitals, which is also in consistent with our previous work for tetra(2-thioyl)-1,4,6,8,11,13-hexazapentacene (TTHAP).^[7a] The calculated band positions for all five compounds (Table 2) indicate that the calculated HOMO and LUMO energies and the bandgaps follow the same trend as the experimental results.

With the increase in conjugation, the band gap of these heteroacenes derivatives are in the order $1 \approx 2 < 3 < 4 \approx 5$ from absorption spectra. This is inconsistent with our calculation results, and the decreased band gap is believed to be mainly caused by the decrease in the LUMO levels. Comparing the chemical structure of **4** and **5**, the HOMO level decreased from -5.72 eV to -6.08 eV with the introduction of an electron-deficient nitrogen atom, which could increase the stability of this heteroacene.

Conclusions

In summary, we report a concise method to synthesize five dioxatetraazapentacene derivatives **1–5**. The absorption spectra have relatively larger bandgaps when internal N-containing substituents are present. Cyclic voltammetry measurements demonstrated that compounds **4** and **5** have less negative reduction potentials, which is inconsistent with the DFT simulations, and both might be promising for use as n-type organic semiconductors. Further studies of laterally extended tetraazadioacenes bearing different substituents and their applications in electronic devices are currently underway.

Experimental Section

2,3-Butanedione, 3,4-hexanedione, benzil, 9,10-phenanthrenequinone, 1,10-phenanthroline-5,6-dione and IBX were purchased from commercial sources. All chemicals and solvents were used directly without further purification. 2,3,7,8-Tetraaminodibenzo-1,4-dioxin tetrahydrochloride was synthesized according to a reported procedure.^[15] Solution NMR spectra were recorded on a Bruker Advance 400 spectrometer. Electrochemistry was carried out with a CHI 600C potentiostat, with glassy carbon (diameter: 1.6 mm; area 0.02 cm²), a platinum wire, and Ag/AgCl (Ag/Ag+) as the working, counter, and reference electrodes, respectively. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as the electrolyte in 80 °C in anhydrous DMF under the protection of argon. The potential was externally calibrated against the ferrocene/ferrocenium couple. HRMS (ESI) spectra were recorded on a Waters Q-ToF premierTM mass spectrometer. UV/vis spectra were recorded using a Shimadzu UV-2501 spectrometer. Thermogravimetric analysis (TGA) was carried out on a TA Instrument Q500 Thermogravimetric Analyzer at a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) was carried out under nitrogen on a DSC Q100 instrument from TA Instruments at a scanning rate of 10 °C min⁻¹. The geometry of the heteroacene derivatives were optimized by using DFT calculations (B3LYP/6-31G*).

Synthesis of 2,3,9,10-Tetramethyl-1,4,8,11-tetraaza-6,13-dioxapentacene (1)

2,3,7,8-Tetraaminodibenzo-1,4-dioxin tetrahydrochloride (180 mg, 0.46 mmol) and 2,3-butanedione (0.5 mL, 5.69 mmol) were dissolved in acetic acid (20 mL) containing IBX (5 mg). The solution was heated to reflux for 48 h. After cooling to room temperature, the precipitate was

filtered and washed with chloroform, ethanol, acetone, and tetrahydrofuran, to give **1** (136 mg, 86%) as a light yellow solid; m.p. > 300 °C. ¹H NMR (400 MHz, TFA-*d*): δ = 7.82 (s, 4H), 2.86 ppm (s, 12H). ¹³C NMR (100 MHz, TFA-*d*): δ = 153.82, 145.42, 134.25, 109.81, 18.92 ppm. FT-IR (KBr): $\tilde{\nu}$ = 1483 cm⁻¹ (C=N). HRMS: *m/z*: calcd for C₂₀H₁₇N₄O₂: 345.1352 [*M*+H]⁺; found: 345.1303. Elemental analysis: calcd: C 69.76, H 4.68, N 16.27; found: C 69.81, H 4.72, N 16.24.

Synthesis of 2,3,9,10-tetraethyl-1,4,8,11-tetraaza-6,13-dioxapentacene (2)

2,3,7,8-Tetraaminodibenzo-1,4-dioxin tetrahydrochloride (180 mg, 0.46 mmol) and 3,4-hexanedione (0.5 mL, 4.11 mmol) were dissolved in acetic acid (20 mL) containing IBX (5 mg). The solution was heated to reflux for 48 h. After cooling to room temperature, methanol (30 mL) was added, then the precipitate was filtered and washed with methanol to give **2** (140 mg, 78%) as a light yellow solid; m.p. 289 °C. ¹H NMR (400 MHz, TFA-*d*): δ = 7.92 (s, 4H), 3.25 (q, 8H, *J* = 7.32 Hz), 1.49 ppm (t, 12H, *J* = 7.32 Hz). ¹³C NMR (100 MHz, TFA-*d*) δ = 156.97, 145.39, 134.49, 110.07, 26.20, 10.25 ppm. FT-IR (KBr): $\tilde{\nu}$ = 1483 cm⁻¹ (C=N). HRMS: *m/z*: calcd for C₂₄H₂₅N₄O₂: 401.1978 [*M*+H]⁺; found: 401.1942. Elemental analysis: calcd C 71.98, H 6.04, N 13.99; found: C 71.86, H 6.59; N 13.96.

Synthesis of 2,3,9,10-Tetraphenyl-1,4,8,11-tetraaza-6,13-dioxapentacene (3)

2,3,7,8-Tetraaminodibenzo-1,4-dioxin tetrahydrochloride (180 mg, 0.46 mmol) and benzil (232 mg, 1.1 mmol) were dissolved in acetic acid (20 mL) containing IBX (5 mg). The solution was heated to reflux for 48 h. After cooling to room temperature, the precipitate was filtered and washed with chloroform, ethanol, acetone, and tetrahydrofuran to give **3** (139 mg, 51%) as a brown-yellow solid; m.p. > 300 °C. ¹H NMR (400 MHz, TFA-*d*): δ = 8.08 (s, 4H), 7.55 (t, 4H, *J* = 7.22 Hz), 7.45 (d, 8H, *J* = 7.60 Hz), 7.40 ppm (t, 8H, *J*₁ = 7.22 Hz, *J*₂ = 7.60 Hz). ¹³C NMR (100 MHz, TFA-*d*): δ = 152.77, 146.00, 135.09, 132.62, 130.99, 129.46, 129.06, 110.38 ppm. FT-IR (KBr): $\tilde{\nu}$ = 1472 cm⁻¹ (C=N). HRMS: *m/z*: calcd for C₄₀H₂₅N₄O₂: 593.1978 [*M*+H]⁺; found: 593.1963. Elemental analysis: calcd: C 81.07, H 4.08, N 9.45; found: C 81.01, H 4.12; N 9.41.

Synthesis of 9,12,21,24-Tetraaza-10,23-dioxabenz[*a, c, p, r*]heptacene (4)

2,3,7,8-Tetraaminodibenzo-1,4-dioxin tetrahydrochloride (180 mg, 0.46 mmol) and 9,10-phenanthrenequinone (312.3 mg, 1.5 mmol) were dissolved in acetic acid (20 mL) containing IBX (5 mg). The solution was heated to reflux for 48 h. After cooling to room temperature, the precipitate was filtered and washed with dichloromethane, ethanol, and acetone to give **4** (132 mg, 49%) as a brown yellow solid; m.p. > 300 °C. ¹H NMR (400 MHz, TFA-*d*): δ = 9.11 (d, 4H, *J* = 8.16 Hz), 8.64 (d, 4H, *J* = 8.20 Hz), 8.31 (s, 4H), 7.97 (t, 4H, *J* = 8.16 Hz), 7.82 ppm (t, 4H, *J* = 8.20 Hz). FT-IR (KBr): $\tilde{\nu}$ = 1466 cm⁻¹ (C=N). HRMS: *m/z*: calcd for C₄₀H₂₁N₄O₂: 589.1665 [*M*+H]⁺; found: 589.2099. Elemental analysis: calcd: C 81.62, H 3.42, N 9.52; found: C 81.66, H 3.38, N 9.49.

Synthesis of 4,5,9,12,21,24-Hexaaza-10,23-dioxabenz[*a, c, p, r*]heptacene (5)

2,3,7,8-Tetraaminodibenzo-1,4-dioxin tetrahydrochloride (180 mg, 0.46 mmol) and 1,10-phenanthroline-5,6-dione (315.3 mg, 1.5 mmol) were dissolved in acetic acid (20 mL) containing IBX (5 mg). The solution was heated to reflux for 48 h. After cooling to room temperature, the precipitate was filtered and washed with chloroform, ethanol, acetone, and tetrahydrofuran to give **5** (272 mg, 57%) as a deep-yellow solid; m.p. > 300 °C. ¹H NMR (400 MHz, TFA-*d*): δ = 10.14 (s, 4H), 9.31 (s, 4H), 8.36 (s, 4H), 8.25 ppm (s, 4H). ¹³C NMR (100 MHz, TFA-*d*): δ = 148.44, 146.64, 140.70, 140.32, 138.48, 136.78, 128.08, 127.61, 112.63 ppm. FT-IR (KBr): $\tilde{\nu}$ = 1470 cm⁻¹ (C=N). HRMS: *m/z*: calcd for C₃₆H₁₇N₆O₂: 593.1474 [*M*+H]⁺; found: 593.1013. Elemental analysis: calcd: C 72.97, H 2.72, N 18.91; found: C 72.93, H 2.76, N 18.96.

Acknowledgements

Q.Z. acknowledges the financial support from AcRF Tier 1 (RG 16/12) and Tier 2 (ARC 20/12) from MOE, CREATE program (Nanomaterials for Energy and Water Management) from NRF, and the New Initiative Fund from NTU, Singapore.

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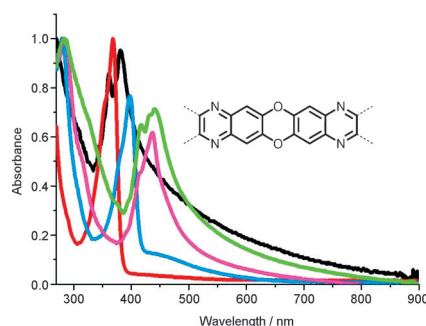
Received: May 20, 2013
Published online: ■■■■■, 0000

FULL PAPER

Dioxapentacenes

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A Concise Method for Synthesizing 1,4,8,11-Tetraaza-6,13-dioxapentacene Derivatives



Give me five: A concise method for preparing five tetraazadioxaacene derivatives is reported. The as-prepared compounds have interesting photophysical and electrochemical properties. Cyclic voltammetry measurements demonstrate that two of the compounds have less negative reduction potentials, which is inconsistent with the results of DFT calculations, and both might be promising for use as active elements in organic electronics.