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Synthesis and Characterization of N,N′-Substituted 15,15,16,16-Tetracyano-6,13-pentacenequinodimethane-2,3,9,10-tetracarboxylic Diimide Derivatives

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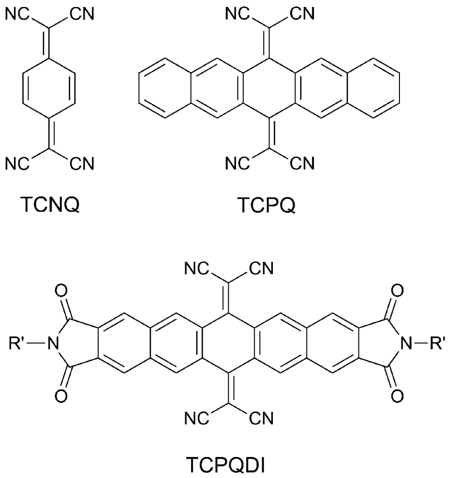
Tetracyanoquinodimethane (TCNQ) and its derivatives have been synthesized and widely used as acceptor molecules in organic optoelectronic devices.[1] 15,15,16,16-Tetracyano-6,13-pentacenequinodimethane (TCPQ) was designed by extending the π system, which leads to a lowering of the intramolecular Coulomb repulsion in the charged species and a more negative value for the first reduction potential ($E_{1/2}{}^{1}=-0.57$ eV vs. standard calomel electrode (SCE)) than TCNQ ($E_{1/2}{}^{1}=0.08$ eV).[2] There is competitive interest to synthesize new ring-fused TCNQ derivatives with high electron affinities. The carboxylic imide unit has been used in many polycyclic aromatic electron-transport materials with good thermal and oxidative stability, high electron affinities, and, in many cases, high electron mobilities.[3] Compared with six-membered carboxylic imide ring derivatives, such as naphthalene and perylene tetracarboxylic diimides, five-membered carboxylic imide ring derivatives have attracted limited attention.



Scheme 1. Chemical structures of TCNQ, TCPQ, and TCPQDI.

Herein we designed a series of cyano-containing electron-acceptor molecules with N-substituted dicarboxylic imides as terminal groups (see TCPQDI in Scheme 1). The molecules have the following characteristics, 1) the extended π system (TCPQ) as the core, 2) two dicyanomethylene and dicarboxylic imide groups as high-electron-affinity units for achieving low LUMO energy levels, and 3) two flexible terminal groups (R′) for enhancing the solubility. Their electrochemical properties have been examined to confirm our molecular design. To our knowledge, this is the first report of the synthesis and the characterization of TCNQ derivatives incorporating fused dicarboxylic imide groups.

The syntheses of compounds PQDI and TCPQDI derivatives are described in Scheme 2. Aniline derivatives with multiple alkoxy substituents (**4a** and **4b**)[4] reacted with maleic anhydride in glacial acetic acid at reflux temprature to afford N-substituted maleimides (**3a** and **3b**) by a simplified process with yields of 65% instead of the normal two-step process.[5] Bromination of 2,3,6,7-tetramethylanthracene-9,10-dione (**2**)[6] with *N*-bromosuccinimide (NBS) and benzoyl peroxide (BPO) as a radical initiator yielded the tetrakis(bromomethyl) derivative **1**. Subsequently, cycloaddition of **1** with N-substituted maleimides (**3a** and **3b**) and subsequent aromatization with NBS/Et_3N afforded pentacenequinone (PQ) derivatives PQDI-OC8 and PQDI-OC10, respectively.[5a] Finally, in the presence of Lehnert's reagent (malononitrile, $TiCl_4$, and pyridine), the corresponding PQ derivatives reacted with malononitrile to afford TCPQ derivatives TCPQDI-OC8 and TCPQDI-OC10, respectively. As previously reported, most π-extended TCNQ derivatives were obtained by using the Lehnert's reagent, and the reaction systems had to be heated at reflux at relatively high temperatures (>100 °C) for a long time (ca. 24 h) due to the poor solubility of the quinone precursors.[2,7] Herein, this reaction could be carried out at room temperature, and

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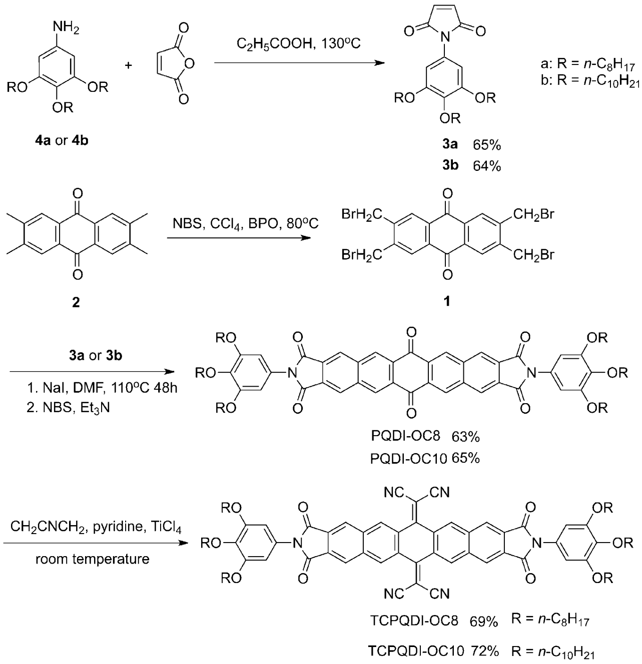

Scheme 2. Synthetic routes to TCPQDI-OC8 and TCPQDI-OC10. DMF = *N*,*N*-dimethylformamide.

the reactions were completed in 8 h in good yield (>70 %), probably due to the good solubility of the PQ precursor and the electron-deficient dicarboxylic imide groups that increase the reactivity of quinone. Because of the flexible alkoxy groups, TCPQDI-OC8, TCPQDI-OC10, PQDI-OC8, and PQDI-OC10 are soluble in common solvents, including ethyl acetate, chloroform, dichloromethane and THF.

TCPQ was synthesized for comparison with TCPQDIs (see Scheme S1 in the Supporting Information) The precursor 6,13-pentacenequinone (**5**)[8] was obtained directly from cycloaddition of hexan-1,4-dione and *o*-phthalaldehyde. Then **5** condensed with malononitrile to give TCPQ in 43 % yield.[2] The above synthesized molecular structures were determined by ^{1}H and ^{13}C NMR spectroscopy along with elemental analysis or high-resolution mass spectrometry. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) revealed that TCPQDI-OC8 and TCPQDI-OC10 melt at 268 and 208 °C, respectively, and are both stable up to 300 °C (see Figures S15–S17 in the Supporting Information)

The optical properties of the synthesized compounds were studied by UV/Vis spectroscopy. The absorption spectra are shown in Figure 1, and the optical data are collected in Table 1. TCPQ was tested for comparison, and has absorption bands from 230 to 470 nm with three distinct absorption peaks, as reported.[2a] For TCPQDI-OC8 and TCPQDI-OC10, there is no red shift in absorption band relative to TCPQ, and the molecular structures are severely deformed from planarity as in TCPQ, the molecular structure of which is distorted as reported previously[2a]. The introduction of tetracarboxylic diimide on the TCPQ core evoked a new strong absorption peak around 292 nm and more intense absorption maxima for TCPQDIs than for TCPQ in the whole absorption band. For PQ derivatives PQDI-OC8 and PQDI-OC10, the absorption intensity of the band that is blue-shifted from 300 to 430 nm is weaker than that of TCPQDI-OC8 and TCPQDI-OC10. As the homologue of PQDI-OC8, PQDI-OC10 displays almost the same absorption spectrum. A similar phenomenon occurs for TCPQDI-OC8 and TCPQDI-OC10 as well. The optical band gaps calculated from the absorption maximum onset are 2.75 eV for TCPQDIs and 2.89 eV for PQDIs, respectively.

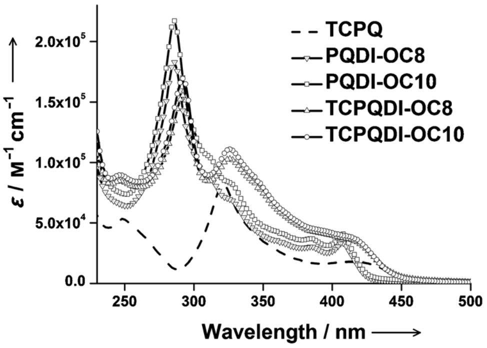

Figure 1. UV/Vis absorption spectra of synthesized compounds in dichloromethane.

Table 1. Optical and Electronic Properties.

Compound	Solution[a]		Experimental				
	λ_{abs} [nm]	ε [$M^{-1}cm^{-1}$][b]	E^{onset}_{red1} [eV]	E^{onset}_{red2} [eV]	E_{HOMO} [eV][e]	E_{LUMO} [eV][c]	ΔE [eV][d]
TCPQDI-OC8	292	155451	−0.31	−1.02	−6.88	−4.13	2.75
TCPQDI-OC10	292	169327	−0.32	−1.06	−6.87	−4.12	2.75
PQDI-OC8	286	182856	−0.60	−1.14	−6.73	−3.84	2.89
PQDI-OC10	286	217139	−0.62	−1.15	−6.71	−3.82	2.89
TCPQ	322	81403	−0.56	−1.04	−6.58	−3.88	2.70

[a] Solution in dichloromethane. [b] Molar extinction coefficient (ε) of the maximum absorption wavelength (λ_{max}). [c] Estimated from the onset of reduction peak ($E_{LUMO} = -(4.44 + E^{onset}_{red1})$ eV). [d] Estimated from onsets of absorption spectra in solution state ($\Delta E = 1240/\lambda_{onset}$ eV). [e] Estimated from ΔE and E_{LUMO} ($E_{HOMO} = -(\Delta E - E_{LUMO})$ eV).[9]

Cyclic voltammetric (CV) measurements for TCPQDI-OC8, TCPQDI-OC10, PQDI-OC8, and PQDI-OC10 were carried out. The results are shown in Figure 2, and the data are collected in Table 1. TCPQ showed the same result as reported.[2] TCPQDI-OC8 and TCPQDI-OC10 showed two reduction waves in the reduction region. The E^{onset}_{red1} of compounds TCPQDI-OC8 and TCPQDI-OC10 (−0.31 and −0.32 eV) were shifted to more positive values compared to TCPQ (−0.57 eV), due to the tetracarboxylic diimide units, which increase the π delocalization and lower the LUMO energy levels. The E^{onset}_{red2} of TCPQDI-OC8 and TCPQDI-OC10 were close to values of TCPQ. The onset E^{onset}_{red1} and E^{onset}_{red2} of TCPQDIs may correspond to the radical

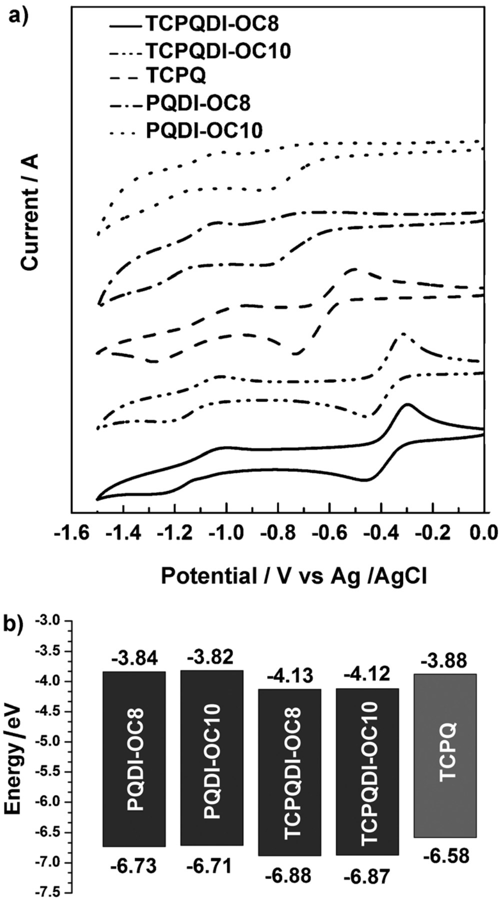

Figure 2. a) Cyclic voltammograms of synthesized compounds in dichloromethane. b) Energy-level diagrams of synthesized compounds.

anion and dianion of the TCPQ unit,[2] whose negative charges are mainly located at two the dicyanomethylene groups.[10] The $E_{\mathrm{red1}}^{\mathrm{onset}}$of compounds PQDI-OC8 and PQDI-OC10 (−0.60 and −0.62 eV) were much more positive than 6,13-pentacenequinone (−1.50 eV)[11] but slightly less negative than TCPQ (−0.56 eV), which may also be ascribed to the introduction of tetracarboxylic diimide that acts as an electron-affinity unit. As shown in Table 1, the LUMO energy levels of TCPQDI-OC8, TCPQDI-OC10, PQDI-OC8, PQDI-OC10, and TCPQ are calculated to be −4.13, −4.12, −3.84, −3.82, and −3.88 eV, whereas the HOMO energy levels are −6.88, −6.87, −6.73, −6.71, and −6.58 eV, respectively. All synthesized compounds exhibit deep HOMO energy levels (below −5.4 eV) to ensure good air stability.[12] The two dicyanomethylene groups and tetracarboxylic diimide groups together make TCPQDI-OC8 and TCPQDI-OC10 present lower LUMO energy levels (<-4.0 eV) and high electron affinities, which is essential to achieve stable electron transport in air.[5a]

According to the results of UV/Vis spectra and CV curves there was a minimal difference for electrochemical properties between the two alkoxy groups. To investigate the relationship between electrochemical properties and molecular structures, the molecules without alkoxy groups (TCPQDI and PQDI) were chosen as model molecules for theoretical calculations at the density functional theory (DFT) B3LYP/6-31G(d,p) level by using Gaussian 09.[13] Their optimized molecular structures and HOMO and LUMO plots are shown in Figure 3b. The optimized geometry of TCPQDI is distorted from planarity, and the molecule adopts a butterfly-type structure, similar to that of TCPQ (Figure 3a).[2] The distortion is due to the strong steric interactions between the cyano groups and the hydrogen atoms at the peri positions. Geometrical and electronic parameters for TCPQ were also calculated, and its HOMO plots are dominated by the orbitals from the aromatic system (pentacene ring), and the coefficients in LUMO plots are offset to the center and dominated by the orbitals from two dicyanomethylene groups. Compared with TCPQ, the HOMO plots of TCPQDI and PQDI are mainly located on the N-substituted groups and have little coefficient of the pentacene rings and the dicyanomethylene groups, while the LUMO incorporates the dicyanomethylene groups, pentacene rings, and tetracarboxylic diimide parts, thus demonstrating efficient LUMO delocalization. The tetracarboxylic diimide groups play an important role in increasing the π delocalization and decreasing the LUMO energy levels. The results were similarly confirmed by CV curves. The HOMO energy levels of TCPQDI and PQDI are calculated to be −6.74 and −6.59 eV, respectively, while their LUMO are fall at −3.96 and −3.31 eV, respectively. The calculated energy gaps are 2.78 and 3.28 eV. These cal-

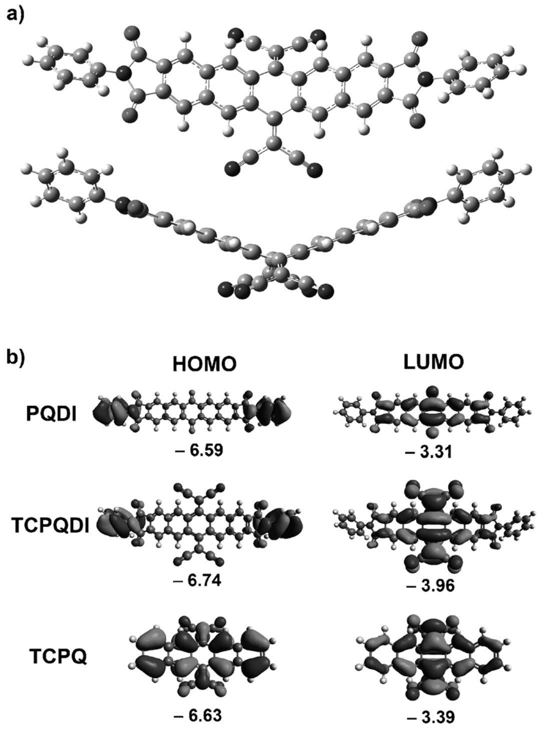

Figure 3. a) Optimized geometry of TCPQDI: top view (top) and side view (bottom); b) HOMO and LUMO (eV) of synthesized compounds according to DFT calculations at the B3LYP/6-31G(d, p) level.

culation data are somewhat close to the experimental values of TCPQDIs and PQDIs estimated from UV/Vis spectra and CV curves.

In summary, we designed and successfully synthesized a series of TCPQDI derivatives that comprise a TCPQ core and two terminal dicarboxylic imide groups and increase the TCNQ family's variety. The flexible alkoxy groups improved molecular solubility, and the highly soluble quinone precursors could react with Lehnert's reagent under mild conditions in good yields. The tetracarboxylic diimide units in TCPQDI derivatives increase π delocalization and lead to lower LUMO energy levels, thus indicating that the incorporation of imide groups is a good strategy to decrease energy levels. Further investigation of TCPQDI derivatives for applications in organic electronics is underway.

Experimental Section

Compounds **1**, **3a**, **3b**, **5**, and TCPQ were obtained as described in the Supporting Information.

General procedure for the synthesis of PQDIs

Dry NaI (1.5 g, 10 mmol) was added to a mixture of **1** (0.73 g, 1 mmol) and N-substituted maleimides (2 mmol) in DMF (30 mL) under nitrogen. The mixture was heated with stirring at 85 °C for 36 h. The reaction mixture turned brown over the course of the reaction. The product mixture was cooled to room temperature and poured into 200 mL of water. Filtration and drying yielded a brown crude product. The crude product, NBS (1.3 g, 7.3 mmol), and benzoyl peroxide (50 mg) were stirred in CCl_4 (50 mL) under nitrogen and then heated at reflux in the dark overnight. The reaction mixture turned red during the course of the reaction. After the mixture had cooled to room temperature, Et_3N (10 mL) was added, and stirring continued for 2 h. The product mixture was poured into water (200 mL), and CH_2Cl_2 (200 mL) was added. The extracted organic layer was dried with anhydrous sodium sulfate. The solvent was evaporated under reduced pressure. The resulting solid was purified by silica gel chromatography (eluent petroleum ether/$CH_2Cl_2 = 3:1$) to give the PQDTs.

N,N′-bis((3′,4′,5′-tris(octyloxy)phenyl)-6,13-pentacenequinone-2,3,9,10-tetracarboxylic diimide (PQDI-OC8)

Following the above procedure **1** in DMF was treated with **3a** (1.16 g, 2 mmol)to give PQDI-OC8 (860 mg, 63 %) as a red powder. m.p.> 300 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 9.06$ (s, 4 H), 8.62 (s, 4 H), 6.67 (s, 4 H), 3.99 (m, 12 H), 1.82 (m, 12 H), 1.48 (m, 12 H), 1.32–1.10 (m, 48 H), 0.86 ppm (m, 18 H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 181.3$, 166.0, 153.4, 138.4, 137.6, 132.2, 131.6, 130.6, 126.6, 126.2, 105.3, 73.6, 69.2, 32.0, 31.9, 30.4, 29.6, 29.4, 29.3, 26.1, 22.7, 22.7, 14.1 ppm; MALDI-TOF MS (*m/z*): 1389.9 $[M+Na]^+$, calcd for $C_{86}H_{114}N_2O_{12}$: 1366.84; elemental analysis (%) calcd for $C_{86}H_{114}N_2O_{12}$: C 75.52, H 8.40, N 2.05; found: C 75.81, H 8.28, N 2.09.

N,N′-bis(3′,4′,5′-tris(decyloxy)phenyl)-6,13-pentacenequinone-2,3,9,10-tetracarboxylic diimide (PQDI-OC10)

Following the above procedure, **1** in DMF was treated with **3b** (1.28 g, 2 mmol) to give PQDI-OC10 (990 mg, 65 %) as a red powder. m.p.> 270 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 9.03$ (2 s, 4 H), 8.63 (2 s, 4 H), 6.67 (s, 4 H), 3.99 (m, 12 H), 1.81 (m, 12 H), 1.46 (m, 12 H), 1.33–1.28 (m, 72 H), 0.88 ppm (m, 18 H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 181.3$, 166.0, 153.4, 138.4, 137.6, 132.2, 131.7, 130.6, 126.6, 126.2, 105.3, 73.6, 69.2, 32.0, 31.9, 30.4, 29.8, 29.7, 29.7, 29.6, 29.4, 29.4, 26.2, 26.1, 22.7, 22.7, 14.1 ppm; MALDI-TOF MS (*m/z*): 1559.0 $[M+Na]^+$, calcd. for $C_{98}H_{138}N_2O_{12}$: 1536.03; elemental analysis (%) calcd for $C_{98}H_{138}N_2O_{12}$: C 76.62, H 9.05, N 1.82; found: C 76.46, H 8.95, N 1.83.

General Procedure for the Synthesis of TCPQDIs

Titanium tetrachloride (0.55 mL, 5 mmol) and then anhydrous pyridine (0.83 mL, 10 mmol) were added dropwise to a solution of PQDIs (0.5 mmol) and malononitrile (0.27 g, 5 mmol) in dry CH_2Cl_2 (40 mL) under nitrogen. The reaction was stirred at room temperature for 8 h. The mixture was poured into water (100 mL) and CH_2Cl_2 was added. The extracted organic layer was dried with anhydrous sodium sulfate. The solvent was evaporated under reduced pressure. The resulting solid was purified by silica gel chromatography (eluent petroleum ether/ $CH_2Cl_2 = 3:1$) to give TCPQDIs.

N,N′-bis(3′,4′,5′-tris(octyloxy)phenyl)-15,15,16,16-tetracyano-6,13-pentacenequinodimethane-2,3,9,10-tetracarboxylic diimide (TCPQDI-OC8)

Following the above procedure PQDI-OC8 (683 mg, 0.5 mmol) was reacted with malononitrile to give TCPQDI-OC8 (495 mg, 69 %) as an orange powder. m.p. = 268 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 8.98$ (s, 4 H), 8.65 (s, 4 H), 6.65 (s, 4 H), 3.99 (m, 12 H), 1.80 (m, 12 H), 1.46 (m, 12 H), 1.32–1.28 (m, 48 H), 0.88 ppm (m, 18 H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 165.8$, 159.2, 153.6, 138.6, 136.1, 131.5, 130.7, 129.2, 126.3, 125.9, 112.8, 105.4, 85.1, 73.8, 69.5, 32.1, 32.0, 30.5, 29.7, 29.6, 29.5, 29.4, 26.2, 22.9, 22.8, 14.3 ppm; MALDI-TOF MS (*m/z*): 1464.0 $[M+H]^+$, 1487.0 $[M+Na]^+$, calcd for $C_{92}H_{114}N_6O_{10}$: 1462.86; elemental analysis (%) calcd for $C_{92}H_{114}N_6O_{10}$: C 75.48, H 7.85, N 5.74; found: C 75.44, H 7.81, N 5.65.

N,N′-bis(3′,4′,5′-tris(decyloxy)phenyl)-15,15,16,16-tetracyano-6,13-pentacenequinodimethane-2,3,9,10-tetracarboxylic diimide (TCPQDI-OC10)

Following the above procedure PQDI-OC10 (768 mg, 0.5 mmol) was treated with malononitrile to give TCPQDI-OC10 (589 mg, 72 %) as an orange powder. m.p. = 208 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 8.99$ (s, 4 H), 8.65 (s, 4 H), 6.65 (s, 4 H), 3.99 (m, 12 H), 1.80 (m, 12 H), 1.44 (m, 12 H), 1.25–1.22 (m, 72 H), 0.88 ppm (m, 18 H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 165.8$, 159.1, 153.6, 138.7, 136.1, 131.5, 130.7, 129.2, 126.3, 125.9, 112.8, 105.4, 85.2, 73.8, 69.5, 32.1, 32.1, 30.5, 29.9, 29.8, 29.8, 29.7, 29.6, 29.5, 26.2, 22.8, 14.3 ppm; MALDI-TOF MS (*m/z*): 1655.0 $[M+Na]^+$, calcd for $C_{104}H_{138}N_6O_{10}$: 1632.05; elemental analysis (%) calcd for $C_{104}H_{138}N_6O_{10}$: C 76.53, H 8.52, N 5.15; found: C 76.28, H 8.51, N 5.38, calcd for: C 76.53, H 8.52, N 5.15.

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Keywords: carboxylic imides · electrochemistry · electronic structure · tetracyanoquinodimethane

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[1] a) R. C. Wheland, E. L. Martin, *J. Org. Chem.* **1975**, *40*, 3101–3109; b) N. Martin, J. A. Navarro, C. Seoane, A. Albert, F. H. Cano, J. Y. Becker, V. Khodorkowsky, E. Harlev, M. Hanack, *J. Org. Chem.* **1992**, *57*, 5726–5730; c) A. M. Kini, D. O. Cowan, F. Gerson, R. Möckel, *J. Am. Chem. Soc.* **1985**, *107*, 556–562; d) N. Martín, J. L. Segura, C. Seoane, *J. Mater. Chem.* **1997**, *7*, 1661–1676.

[2] a) N. Martin, R. Behnisch, M. Hanack, *J. Org. Chem.* **1989**, *54*, 2563–2568; b) N. Martin, M. Hanack, *J. Chem. Soc. Chem. Commun.* **1988**, 1522–1524.

[3] a) F. Würthner, M. Stolte, *Chem. Commun.* **2011**, *47*, 5109–5115; b) X. Zhan, A. Facchetti, S. Barlow, T. J. Marks, M. A. Ratner, M. R. Wasielewski, S. R. Marder, *Adv. Mater.* **2011**, *23*, 268–284.

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[4] C. V. Yelamaggad, A. S. Achalkumar, D. S. S. Rao, S. K. Prasad, *J. Org. Chem.* **2007**, *72*, 8308–8318.

[5] a) Z. Wang, C. Kim, A. Facchetti, T. J. Marks, *J. Am. Chem. Soc.* **2007**, *129*, 13362–13363; b) D. Fleš, R. Vuković, A. E. Kuzmić, G. Bogdanić, V. Piližta, D. Karlović, K. Markuš, K. Wolsperger, D. Vikić-Topić, *Croat. Chem. Acta* **2003**, *76*, 69–74.

[6] C. E. Godinez, G. Zepeda, C. J. Mortko, H. Dang, M. A. Garcia-Garibay, *J. Org. Chem.* **2004**, *69*, 1652–1662.

[7] S. Yamaguchi, T. Hanafusa, T. Tanaka, M. Sawada, K. Kondo, M. Irie, H. Tatemitsu, Y. Sakata, S. Misumi, *Tetrahedron Lett.* **1986**, *27*, 2411–2414.

[8] a) V. H. Gessner, T. D. Tilley, *Org. Lett.* **2011**, *13*, 1154–1157; b) C. Pramanik, G. P. Miller, *Molecules* **2012**, *17*, 4625–4633; c) N. Vets, M. Smet, W. Dehaen, *Tetrahedron Lett.* **2004**, *45*, 7287–7289.

[9] C. Du, Y. Guo, Y. Liu, W. Qiu, H. Zhang, X. Gao, Y. Liu, T. Qi, K. Lu, G. Yu, *Chem. Mater.* **2008**, *20*, 4188–4190.

[10] F. Gerson, R. Heckendorn, D. O. Cowan, A. M. Kini, M. Maxfield, *J. Am. Chem. Soc.* **1983**, *105*, 7017–7020.

[11] Q. Tang, Z. Liang, J. Liu, J. Xu, Q. Miao, *Chem. Commun.* **2010**, *46*, 2977–2979.

[12] H. G. Kim, S. B. Jo, C. Shim, J. Lee, J. Shin, E. C. Cho, S.-G. Ihn, Y. S. Choi, Y. Kim, K. Cho, *J. Mater. Chem.* **2012**, *22*, 17709–17717.

[13] Gaussian 09, Revision A.02, M. J. Frisch et al. Gaussian, Inc., Wallingford, CT, **2009**.

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