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## Synthesis of benzo[*de*]isoquino[1,8-*gh*]quinolines and light-induced electron transfer in their composites with conductive polymer poly(3-hexylthiophene)

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Benzo[de]isoquino[1,8-gh]quinolines were prepared by the reaction between 1,5-diethynyl-9,10-anthraquinones and urea in DMF. Light-induced electron transfer from regioregular poly(3-hexylthiophene) to the synthesized molecules was detected by an EPR spectroscopy technique.

In most organic photovoltaic cells, fullerenes are used as an acceptor.<sup>1</sup> Meanwhile a search for simple and inexpensive acceptor materials with molecules of small size is progressing.<sup>2</sup> At present, the variety of approved substances is small and represented mostly by perylene (perylenediimide) derivatives.<sup>3</sup> Perylene derivatives are also used in other devices, such as organic field-effect transistors.<sup>4</sup> Here, we report on a new synthesis of benzo[*de*]-isoquino[1,8-*gh*]quinolines, perylene 1,7-diazo analogues, which are promising acceptor materials for organic photovoltaics. Note that the reported procedures for synthesizing these compounds are rather sparse and laborious.<sup>5</sup>

Compounds  $1^{\dagger}$  were obtained by heterocyclization of 1,5-dialkynyl-9,10-anthraquinones  $2^{\ddagger}$  with an excess of urea in DMF

<sup>†</sup> Combustion analysis was performed with a CHN-analyzer (Model 1106, Carlo Erba). The NMR spectra were recorded on a Bruker AV 400 spectrometer (400.13 MHz for <sup>1</sup>H, 100 MHz for <sup>13</sup>C) in CDCl<sub>3</sub>. Melting points were determined with a Kofler apparatus. Mass spectra were obtained on a Thermo Electron Corporation DFS mass spectrometer (70 eV) using direct injection, the temperature of the ionization chamber was 220–270 °C. The IR spectra were recorded in KBr pellets on a Bruker Vector 22 instrument. Column chromatography was performed on 60 (Merck) and the Silufol UV-254 plates were used for TLC analysis.

2,8-Di-R-benzo[de]isoquino[1,8-gh]quinolines 1 (general procedure). A mixture of 1,5-dialkynyl-9,10-anthraquinone 2 (0.4 mmol) and urea (4 g, 66.7 mmol) in 2.8 ml of DMF was boiled for 2 h. A mixture of toluene (50 ml) and water (50 ml) was then added, the organic layer was separated, dried over MgSO<sub>4</sub> and evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on  $Al_2O_3$  (elution with toluene). Subsequent recrystallization gave pure compounds.

2,8-Dibutylbenzo[de]isoquino[1,8-gh]quinoline **1a**. Yield 65 mg (45%), mp 166–167 °C (toluene). <sup>1</sup>H NMR,  $\delta$ : 1.01 (t, 6 H, 2 Me, J 7.4 Hz), 1.50 (m, 4H, 2 CH<sub>2</sub>), 1.90 (m, 4H, 2 CH<sub>2</sub>), 2.99 (t, 2H, 2 CH<sub>2</sub>Pr, J 7.7 Hz), 7.39 (s, 2H, 2 H<sub>Py</sub>), 7.72 (m, 4H, 4 H<sub>Ar</sub>), 8.88 (m, 2 H, 2 H<sub>Ar</sub>). <sup>13</sup>C NMR,  $\delta$ : 14.2, 22.7, 32.1, 38.2 (2 Bu), 118.2, 123.1, 123.5, 127.8, 130.8, 132.8, 137.5, 150.1, 156.8 (C<sub>Ar</sub>). Found (%): C, 85.19; H, 7.03; N, 7.55. Calc. for C<sub>26</sub>H<sub>26</sub>N<sub>2</sub> (%): C, 85.21; H, 7.15; N, 7.64. HRMS, *m*/*z*: 366.2087 [M]<sup>+</sup> (calc. for C<sub>26</sub>H<sub>26</sub>N<sub>2</sub>, *m*/*z*: 366.2091).

2,8-Dihexylbenzo[de]isoquino[1,8-gh]quinoline **1b**. Yield 60 mg (35%), mp 143–144 °C (toluene–light petroleum). <sup>1</sup>H NMR,  $\delta$ : 0.91 (t, 6H, 2Me, J 7.3 Hz), 1.37 [m, 8H, 2(CH<sub>2</sub>)<sub>2</sub>], 1.46 (m, 4H, 2CH<sub>2</sub>), 1.91 (m, 4H, 2CH<sub>2</sub>), 2.98 [t, 4H, 2CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>Me, J 7.8 Hz], 7.39 (s, 2H, H<sub>Py</sub>), 7.73 (m, 4H, 4H<sub>At</sub>), 8.88 (m, 2H, 2H<sub>At</sub>). <sup>13</sup>C NMR,  $\delta$ : 14.3, 22.8, 29.3, 29.9, 32.0, 38.5 (hexyl), 118.2, 123.1, 123.5, 127.8, 130.8, 132.8, 137.5, 150.1, 156.9 (C<sub>At</sub>). Found (%): C, 85.70; H, 8.31; N, 6.65. Calc. for C<sub>26</sub>H<sub>26</sub>N<sub>2</sub> (%): C, 85.26; H, 8.11; N, 6.63. HRMS, *m/z*: 422.2724 [M]<sup>+</sup> (calc. for C<sub>30</sub>H<sub>34</sub>N<sub>2</sub>, *m/z*: 422.2717).



Scheme 1 Reagents and conditions: i,  $RC \equiv CCu$ , Py, 75 °C, 25 min; ii,  $(NH_2)_2CO$ , DMF, 153 °C, 2 h.

upon boiling (Scheme 1). The optimal reaction time was 2 h, the yields of target heterocycles 1 were from 35 to 47%.

The temperature and the high excess of urea were the crucial reaction factors. Heating DMF provided sufficient urea dissolu-

2,8-Bis(prop-2-yloxymethyl)benzo[de]isoquino[1,8-gh]quinoline **1c**. Yield 70 mg (44%), mp 174–175 °C (light petroleum). <sup>1</sup>H NMR,  $\delta$ : 1.35 (d, 12 H, 4 Me, *J* 6.0 Hz), 3.89 (m, 2 H, 2 CHMe<sub>2</sub>), 4.87 (s, 4 H, 2 CH<sub>2</sub>), 7.73 (s, 2 H, H<sub>Py</sub>), 7.76 (m, 2 H, 2 H<sub>Ar</sub>), 7.81 (m, 2 H, 2 H<sub>Ar</sub>), 8.86 (m, 2 H, 2 H<sub>Ar</sub>). <sup>13</sup>C NMR,  $\delta$ : 22.4 (2 Me), 71.3 (2 CH<sub>2</sub>), 72.1 (CHMe<sub>2</sub>), 117.1, 123.7, 124.0, 128.6, 130.9, 132.6, 137.5, 150.0, 153.9 (C<sub>Ar</sub>). Found (%): C, 78.29; H, 6.25; N, 7.14. Calc. for C<sub>26</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub> (%): C, 78.36; H, 6.58; N, 7.03. HRMS, *m/z*: 398.1984 [M]<sup>+</sup> (calc. for C<sub>26</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>, *m/z*: 398.1989).

2,8-Bis(butoxymethyl)benzo[de]isoquino[1,8-gh]quinoline 1d. Yield 80 mg (47%), mp 122–123 °C (toluene–light petroleum). <sup>1</sup>H NMR,  $\delta$ : 0.98 (t, 6H, 2Me, J 7.4 Hz), 1.50 (m, 4H, 2CH<sub>2</sub>), 1.73 (m, 4H, 2CH<sub>2</sub>), 3.70 (t, 4H, 2CH<sub>2</sub>Pr, J 6.7 Hz), 4.85 (s, 4H, 2CH<sub>2</sub>OBu), 7.70 (s, 2H, H<sub>Py</sub>), 7.75 (m, 2H, 2H<sub>Ar</sub>), 7.81 (dd, 2H, 2H<sub>Ar</sub>, J 1.1 and 8.2 Hz), 8.87 (dd, 2H, 2H<sub>Ar</sub>, J 1.2 and 7.2 Hz). <sup>13</sup>C NMR,  $\delta$ : 14.2, 19.6, 32.1 (Pr), 71.2 (OCH<sub>2</sub>Pr), 74.0 (CH<sub>2</sub>OBu), 117.2, 123.8, 124.1, 128.6, 130.9, 132.5, 137.4, 150.1, 153.4 (C<sub>Ar</sub>). Found (%): C, 79.67; H, 7.25; N, 6.40. Calc. for C<sub>28</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub> (%): C, 78.84; H, 7.09; N, 6.57. HRMS, *m/z*: 426.2304 [M]<sup>+</sup> (calc. for C<sub>28</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>, *m/z*: 426.2302).

<sup>‡</sup> 1,5-Dialkynyl-9,10-anthraquinones **2** (general procedure). A mixture of 1,5-diiodo-9,10-anthraquinone (1.1 mmol) and copper acetylides (2.5 mmol) in 15 ml of pyridine was stirred under stream of argon at 75 °C for 25 min. Then ethyl acetate (100 ml) was added, the organic layer was washed with 5% aqueous NH<sub>3</sub> (50 ml) and water (100 ml), dried over MgSO<sub>4</sub>. The crude product was purified by column chromatography on SiO<sub>2</sub> (elution with toluene). Subsequent recrystallization gave pure compounds **2a–d**. tion as compared with most of the organic solvents (alcohols, pyridine, *etc.*) tested. The technique used to perform reaction in liquid urea<sup>6</sup> failed to provide satisfactory yields of target products.

The choice of substituents R was determined mainly by the need to get products **1** with acceptable solubility and melting temperature which is of major importance for producing conducting films with optimal morphology and electric characteristics. The effect of substituents R on the yield and the time of reaction between bis-alkynes **2** and urea was minor. Compounds **2** are poorly examined<sup>7</sup> and represent polyfunctional electrophilic substrates that are sensitive to thermal and chemical action. Some of these compounds are even unstable upon chromatography on Al<sub>2</sub>O<sub>3</sub> and long storage. Probably, these characteristics of bis-alkynes **2** are responsible for the undesired negative processes during their synthesis and transformation with urea which undergoes complex destruction upon heating.

Bis-alkynes **2** were synthesized by the Castro method<sup>8</sup> from 1,5-diiodo-9,10-anthraquinone<sup>9</sup> and the corresponding copper acetylides in pyridine at 75 °C (see Scheme 1). After 0.5 h, the yield of products **2** was 63-84%.

*1,5-Di(octyn-1-yl)-9,10-anthraquinone* **2b**. Yield 300 mg (64%), mp 105–106 °C (light petroleum). <sup>1</sup>H NMR,  $\delta$ : 0.92 (t, 6 H, 2Me, *J* 7.1 Hz), 1.36 [m, 8 H, 4 (CH<sub>2</sub>)<sub>2</sub>], 1.55 (m, 4 H, 2 CH<sub>2</sub>), 1.72 (m, 4 H, 2 CH<sub>2</sub>), 2.59 [t, 4H, 2 CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Me, *J* 7.1 Hz], 7.67 (t, 2H, 2H<sub>Ar</sub>, *J* 7.8 Hz), 7.82 (dd, 2H, 2 H<sub>Ar</sub>, *J* 1.3 and 7.8 Hz), 8.28 (dd, 2H, 2 H<sub>Ar</sub>, *J* 1.3 and 7.8 Hz), 8.28 (dd, 2H, 2 H<sub>Ar</sub>, *J* 1.3 and 7.8 Hz), 8.29, 31.6 (2hexyl), 80.3, 98.4 (2C≡C), 124.4, 127.1, 132.72, 133.0, 135.3, 140.4 (C<sub>Ar</sub>), 182.1 (2C=O). IR ( $\nu/cm^{-1}$ ): 2953, 2936, 2924, 2853 (hexyl), 2220 (C≡C), 1672 (C=O). Found (%): C, 85.84; H, 7.57. Calc. for C<sub>30</sub>H<sub>32</sub>O<sub>2</sub> (%): C, 84.87; H, 7.60.

*1,5-Bis*[*3-(prop-2-yloxy)propyn-1-yl*]*-9,10-anthraquinone* **2c**. Yield 370 mg (84%), mp 119–120 °C (light petroleum). <sup>1</sup>H NMR,  $\delta$ : 1.29 (d, 12 H, 4 Me, *J* 6.2 Hz), 4.05 (m, 2 H, 2 CHMe<sub>2</sub>), 4.55 (s, 4 H, 2 CH<sub>2</sub>), 7.71 (t, 2 H, 2 H<sub>Ar</sub>, *J* 7.8 Hz), 7.88 (dd, 2 H, 2 H<sub>Ar</sub>, *J* 1.2 and 7.8 Hz), 8.31 (dd, 2 H, 2 H<sub>Ar</sub>, *J* 1.3 and 7.8 Hz). <sup>13</sup>C NMR,  $\delta$ : 22.1 (2 Me), 56.5 (2 CHMe<sub>2</sub>), 71.0 (2 CH<sub>2</sub>), 84.8, 93.2 (2 C=C), 123.0, 127.8, 132.8, 133.2, 135.1, 140.3 (C<sub>Ar</sub>), 181.7 (2 C=O). IR ( $\nu$ /cm<sup>-1</sup>): 2970, 2936, 2903, 2872 (CH<sub>2</sub>OCHMe<sub>2</sub>), 2220 (C=C), 1672 (C=O). Found (%): C, 78.72; H, 5.79. Calc. for C<sub>26</sub>H<sub>24</sub>O<sub>4</sub> (%): C, 77.98; H, 6.04.

*I*,5-*B*is(3-butoxypropyn-1-yl)-9,10-anthraquinone **2d**. Yield 300 mg (64%), mp 120–121 °C (light petroleum). <sup>1</sup>H NMR, δ: 0.97 (t, 6H, 2Me, *J*7.4 Hz), 1.46 (m, 4H, 2 CH<sub>2</sub>), 1.68 (m, 4H, 2 CH<sub>2</sub>), 3.73 (t, 4H, 2 CH<sub>2</sub>Pr, *J* 6.7 Hz), 4.54 (s, 4H, 2 CH<sub>2</sub>OBu), 7.72 (t, 2H, 2H<sub>Ar</sub>, *J* 7.8 Hz), 7.88 (dd, 2H, 2H<sub>Ar</sub>, *J* 1.3 and 7.8 Hz), 8.32 (dd, 2H, 2H<sub>Ar</sub>, *J* 1.3 and 7.8 Hz), 8.32 (dd, 2H, 2H<sub>Ar</sub>, *J* 1.3 and 7.8 Hz), 1<sup>3</sup>C NMR, δ: 14.1, 19.5, 31.9, 59.2 (2Bu), 70.3 (2CH<sub>2</sub>O), 85.3, 92.9 (2C≡C), 123.1, 127.8, 132.9, 133.2, 135.2, 140.3 (C<sub>Ar</sub>), 181.7 (2C=O). Found (%): C, 78.72; H, 6.38. Calc. for C<sub>28</sub>H<sub>28</sub>O<sub>4</sub> (%): C, 78.48; H, 6.59. <sup>§</sup> UV-VIS spectra were obtained on an Ocean Optics USB-650UV spectrometer. Extinction coefficient was determined for chloroform solutions of compounds **1a–d** as  $3.9 \times 10^4$ ,  $3.1 \times 10^4$ ,  $2.1 \times 10^4$  and  $2.7 \times 10^4$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>, respectively. The spectra lineshapes coincide both for **1a,b** and for **1c,d** (data not showed).

<sup>¶</sup> EPR spectra were obtained using an X-band ELEXSYS ESP-580 EPR spectrometer equipped with a dielectric cavity (Bruker ER 4118 X-MD-5) at room temperature, mw frequency 9.6033 GHz, mw power 6.3 mW, modulation amplitude 3 G. LiF standard was used to determine the *g*-value of EPR line. To prepare an EPR sample, chloroform solution of **1c** and regioregular poly(3-hexylthiophene), P3HT (Aldrich), was prepared at 3:1 weight ratio in the tube with 4.5 mm inner diameter, and chloroform was evaporated. The sample in an EPR cavity was illuminated by laser diode light with 660 nm wavelength, light power was about 1 mW.



Figure 1 Optical absorption spectra of (1) 1a and (2) 1c in chloroform.

Figure 1 shows UV-VIS spectra of solutions of compounds **1a** and **1c** in chloroform.<sup>8</sup> The lineshapes of the spectra coincide but with a slight shift in positions of the spectrum maxima:  $\lambda_{\text{max}} = 449$  and 444 nm for **1a** and **1c**, respectively. The energy gap  $E_g = 2.4$  eV between the HOMO and LUMO levels for **1** was determined from the absorption edge (525 nm).

Conducting polymer regioregular poly(3-hexylthiophene) (P3HT) is widely applied as p-type semiconductor in bulk heterojunction photovoltaic cells.<sup>10</sup> P3HT has small energy gap  $E_g =$ = 1.7 eV, which corresponds to a 760 nm optical absorption edge.<sup>11</sup> Figure 2 represents EPR spectra of the composite consisting of 1c and P3HT.<sup>¶</sup> When the sample is irradiated by continuous (660 nm) laser light, the intensity of EPR spectrum line is increased as compared with the dark line. Commonly light-induced EPR signal in the donor-acceptor composites appear from charge carriers, from cation radicals in donor and anion radicals in acceptor phase.12 Appearance of these radicals may cause photocurrent generation in a photoelectric cell.<sup>13</sup> On absorption of 660 nm light by P3HT the light induced electron transfer occurs: EPR spectrum consists of two lines with homogeneous broadening. The most intensive line has width of about 3 G, g-factor of 2.0023±0.0001; on this basis it can be interpreted as the line of P3HT<sup>+</sup> radical cation.<sup>14</sup> The other lightinduced EPR signal is weaker and slightly shifted to low-field and possibly originates from 1c<sup>-</sup> radical anion. This line has a large linewidth (~10 G) due to hyperfine splitting on nitrogen and hydrogen nuclei of the  $\pi$ -conjugated acceptor part of the molecule.

In conclusion, heterocyclization of 1,5-dialkynyl-9,10-anthraquinones with excess of urea in boiling DMF affords 2,8-bis-R-benzo[de]isoquino[1,8-gh]quinolines. Light-induced electron transfer from P3HT to **1c** molecules was detected by EPR spectroscopy.



**Figure 2** EPR spectra of composite 1c: P3HT obtained from (1) irradiated sample and (2) in the dark, and (3) light-induced EPR signal.

*<sup>1,5-</sup>Di*(*hexyn-1-yl*)-9,10-anthraquinone **2a**. Yield 254 mg (63%), mp 114–115 °C (light petroleum). <sup>1</sup>H NMR,  $\delta$ : 0.99 (t, 6H, 2Me, *J*7.2 Hz), 1.57 (m, 4H, 2 CH<sub>2</sub>), 1.71 (m, 4H, 2 CH<sub>2</sub>), 2.60 (t, 4H, 2 CH<sub>2</sub>Pr, *J* 7.1 Hz), 7.67 (t, 2H, 2H<sub>Ar</sub>, *J* 7.8 Hz), 7.82 (dd, 2H, 2H<sub>Ar</sub>, *J* 1.2 and 7.8 Hz), 8.28 (dd, 2H, 2H<sub>Ar</sub>, *J* 1.2 and 7.8 Hz). <sup>13</sup>C NMR,  $\delta$ : 13.9, 20.0, 22.3, 30.9 (2Bu), 80.2, 98.3 (2C=C), 124.4, 127.1, 132.7, 133.0, 135.3, 140.4 (C<sub>Ar</sub>), 182.1 (2C=O). IR ( $\nu/cm^{-1}$ ): 2953, 2928, 2868 (Bu), 2216 (C=C), 1674 (C=O). Found (%): C, 85.20; H, 6.34. Calc. for C<sub>26</sub>H<sub>24</sub>O<sub>2</sub> (%): C, 84.75; H, 6.57.

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