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ELECTROCHEMICAL CAPTURE AND RELEASE OF CO₂ IN AQUEOUS ELECTROLYTES USING AN ORGANIC SEMICONDUCTOR ELECTRODE

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Synthetic procedures and characterization:

The synthetic route to 2,7-bis(4-(2-(2-ethylhexyl)thiazol-4-yl)phenyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (NBI-thiazole) and synthetic procedures are presented below.
3-ethylheptane nitrile (1)

2.73 g (0.042 mol) of KCN, 7.73 g (0.056 mol) of K$_2$CO$_3$ and 150 ml of DMF were added to a 250 ml three-neck-round-bottom flask. The mixture was heated to 50 °C and 5.43 g (0.028 mol) of 2-ethylhexyl bromide was added dropwise. The reaction mixture was stirred at 90 °C for 24 hours. Then, after cooling down to room temperature it was poured into 150 ml of water and extracted with toluene. The collected organic phases were dried over MgSO$_4$. Then, the organic solvent was removed yielding 3.00 g (75 %) of colorless oil, that was used in the next step without further purification.

$^1$HNMR (200 MHz, CDCl$_3$), $\delta$ [ppm]: 2.34 (d, J=6.00 Hz, 2H), 1.70-1.20 (m, 9H), 0.96-0.88 (m, 6H).

$^{13}$CNMR (125 MHz, CDCl$_3$), $\delta$ [ppm]: 120.03 (1C), 36.83 (1C), 31.25 (1C), 28.56 (1C), 26.49 (1C), 22.51 (1C), 20.43 (1C), 14.00 (1C), 10.08 (1C).

3-ethylheptane amide (2)

An aqueous solution of NaOH (1 M, 25 ml) was added to a stirred solution of 0.50 g (0.0036 mol) of 3-ethylheptane nitrile (1) in ethyl alcohol (50 ml). An aqueous solution of H$_2$O$_2$ (30 %, 25 ml) was then added dropwise. After being stirred for 1 h at room temperature the reaction mixture was poured into 50 ml of water and extracted with CHCl$_3$ (3×30 ml). The combined organic phases were dried over MgSO$_4$ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel, using CHCl$_3$ as an eluent yielding 0.50 g (89 %) of white crystalline solid.

$^1$HNMR (500 MHz, CDCl$_3$), $\delta$ [ppm]: 5.80 (bs, 1H), 5.49 (bs, 1H), 2.13 (d, J=5.00 Hz, 2H), 1.83-1.76 (m, 1H), 1.44-1.24 (m, 8H), 0.90-0.87 (m, 6H).

$^{13}$CNMR (125 MHz, CDCl$_3$), $\delta$ [ppm]: 175.63 (1C), 40.70 (1C), 36.64 (1C), 32.91 (1C), 28.77 (1C), 26.11 (1C), 22.97 (1C), 14.09 (1C), 10.75 (1C).

3-ethylheptane amide (2) to 3-ethylheptane thioamide (3).
2.00 g (0.0130 mol) of (2) and 2.63 g (0.0065 mol) of Lawesson’s reagent were dissolved in 150 ml of toluene. The reaction mixture was heated in 70-80 °C for 10 h. The progress of the reaction was controlled by TLC. After complete disappearance of the substrate, the reaction mixture was cooled down to room temperature and the solvent was evaporated. The crude product was purified by column chromatography on silica gel, using toluene and the mixture of toluene and CHCl₃ (9:1, v/v) as eluents yielding 1.50 g (67 %) of orange oil.

1H NMR (200 MHz, CDCl₃), δ [ppm]: 7.74 (bs, 1H), 6.88 (bs, 1H), 2.57 (d, J=7.20 Hz, 2H), 2.05-1.85 (m, 1H), 1.45-1.20 (m, 8H), 0.89 (t, J=7.40 Hz, 6H).

13C NMR (125 MHz, CDCl₃), δ [ppm]: 198.03 (1C), 36.95 (1C), 31.18 (1C), 30.56 (1C), 28.52 (1C), 27.49 (1C), 22.63 (1C), 14.08 (1C), 11.09 (1C).

2-(2-ethylhexyl)-4-(4-nitrophenyl)-1,3-thiazole (4)

1.50 g (0.0087 mol) of (3) and 2.50 g (0.0104 mol) of 2-bromo-4’-nitroacetophenone were dissolved in 100 ml of acetone. The reaction mixture was stirred at room temperature for 12 hours and the progress of the reaction was controlled by TLC. After complete disappearance of the substrate, the solvent was removed. The crude product was purified by column chromatography (silica gel, toluene) yielding 900 mg (32 %) of yellow oil.

1H NMR (200 MHz, CDCl₃), δ [ppm]: 8.26 (dt, J=2.20 Hz, J=9.00 Hz, 2H), 8.05 (dt, J=2.40 Hz, J=6.80 Hz, 2H), 7.56 (s, 1H), 3.00 (d, J=7.00 Hz, 2H), 1.98-1.80 (m, 1H), 1.50-1.21 (m, 8H), 0.97-0.84 (m, 6H).

13C NMR (125 MHz, CDCl₃), δ [ppm]: 170.01 (1C), 148.07 (2C), 139.21 (1C), 132.01 (1C), 127.95 (2C), 116.23 (2C), 114.99 (1C), 43.87 (1C), 36.74 (1C), 30.07 (1C), 28.96 (1C), 27.05 (1C), 22.64 (1C), 14.03 (1C), 11.07 (1C).

4-[2-(2-ethylhexyl)-1,3-thiazol-4-yl]aniline (5)

900 mg (0.003 mol) of (4) and 0.100 g of Pd/C were suspended in 25 ml of ethyl alcohol. The mixture was heated to reflux and 2 ml of hydrazine monohydrate was added dropwise. After 6 hours the reaction mixture was cooled down to room temperature, filtered (to remove Pd/C) and the solvent was evaporated. The crude product was purified by column chromatography (silica gel, CHCl₃), yielding 800 mg (93 %) of colorless oil.

1H NMR (200 MHz, CDCl₃), δ [ppm]: 7.70 (dt, J=2.00 Hz, J=8.60 Hz, 2H), 7.12 (s, 1H), 6.70 (dt, J=2.00 Hz, J=8.60 Hz, 2H), 3.74 (s, 2H), 2.97 (d, J=6.80 Hz, 2H), 1.90-1.75 (m, 1H), 1.49-1.20 (m, 8H), 0.95-0.80 (m, 6H).

13C NMR (125 MHz, CDCl₃), δ [ppm]: 168.71 (1C), 149.80 (2C), 131.10 (1C), 127.05 (2C), 116.33 (1C), 113.01 (2C), 42.38 (1C), 36.94 (1C), 31.49 (1C), 28.70 (1C), 26.09 (1C), 21.99 (1C), 14.03 (1C), 11.45 (1C).

2,7-bis(4-(2-(2-ethylhexyl)thiazol-4-yl)phenyl)benzo[lnmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (NBIT)

375 mg (0.0014 mol) of 1, 4, 5, 8-naphthalenetetracarboxylic acid dianhydride and 614 mg (0.0028 mol) of zinc acetate dihydrate were stirred in DMF (50 ml) for 20 min. Then 800 mg (0.0028 mol) of (5) was added and the mixture was heated in 160 °C overnight. The crude product was poured into 50 ml of water, filtered and washed with methanol. The crude product was dried in air and purified according to the multistep purification procedure: (1) preliminary column chromatography on silica gel, using CHCl₃ and 1.5-2 % solution of methyl alcohol in CHCl₃ as eluents; (2) the obtained solid was precipitated with methyl alcohol from CHCl₃ and CH₂Cl₂; (3) column chromatography on silica gel, using CHCl₃ as an eluent yielding 230 mg (20 %) of yellow solid.
$^1$HNMR (500 MHz, CDCl$_3$), $\delta$ [ppm]: 8.85 (s, 4H), 8.11 (dt, $J_1$=5.00 Hz, $J_2$=10.00 Hz, 4H), 7.44 (s, 2H), 7.39 (dt, $J_1$=5.00 Hz, $J_2$=10.00 Hz, 4H), 3.02 (d, $J$=5.00 Hz, 4H), 1.88 (sep, $J$=5.00 Hz, 2H), 1.47-1.25 (m, 16H), 0.96-0.89 (m, 12H).

$^{13}$CNMR (125 MHz, CDCl$_3$), $\delta$ [ppm]: 170.75 (2C), 162.95 (2C), 153.92 (2C), 135.67 (2C), 133.90 (2C), 131.48 (2C), 128.79 (4C), 127.51 (2C), 127.22 (4C), 127.06 (4C), 112.99 (4C), 40.52 (2C), 37.64 (2C), 32.53 (2C), 28.81 (2C), 25.80 (2C), 22.98 (2C), 14.14 (2C), 10.83 (2C).

**Electrode preparation and electrochemical characterization:**

10mg of NBIT was dissolved in 1mL chlorobenzene to obtain a 12.4 mM solution. Glassy carbon plates were first mechanically polished with alumina to remove any surface impurities and then washed thoroughly with distilled water and 2-propanol respectively. Later the glassy carbon plates were sonicated in deionized water for 30 min. The cleaning procedure was completed by electrochemical cleaning in 0.1M HClO$_4$ via potentiodynamic cycling. A thin film of NBIT was spin coated from its solution at 1000 rpm and dried under N$_2$ flow.

All electrochemical characterizations were done in 0.1M Na$_2$SO$_4$ under inert atmosphere (under N$_2$ or CO$_2$). NBIT coated glassy carbon electrode was used as working electrode with Pt plate acting as counter electrode and a Ag/AgCl (3M KCl) as the reference electrode in an H-cell geometry.

![Figure S1](image.png)

Figure S1. Three consecutive cyclic voltammograms showing the electrochemical behavior of NBI-thiazole on glassy carbon (WE). Electrolyte was 0.1M Na$_2$SO$_4$ in water. Pt foil was used as counter electrode while Ag/AgCl (3M KCl) was utilized reference electrode.
**Figure S2.** Cyclic stability of NBIT in 0.1M Na$_2$SO$_4$ under CO$_2$ atmosphere.

**Figure S3.** Visual representation of molecular frontier orbitals of the NBIT core.
**Figure S4.** CV of NBIT before (red line), after CO$_2$ capture (blue line) and after CO$_2$ release (green line).

**Figure S5.** Calibration curve for the determination of extinction coefficient of NBI-thiazole. Different concentrations were obtained by gradual dilution of 1mM solution of NBI-thiazole in chlorobenzene with chlorobenzene.
Figure S6. Corresponding equivalent electrical circuits for EIS data fitting of NBIT under (a) Ar atmosphere and (b) CO$_2$ atmosphere at -1.0V and below, consisting of the ohmic resistance of the electrolyte solution ($R_s$), the double layer capacitance ($C_{dl}$) and the charge transfers resistance ($R_{ct}$). While under Ar saturation the EIS data can be well explained by a single R/C element in series with the $R_s$,[1,2] two R/C elements have to be used, in series with the $R_s$, to fit the spectra under CO$_2$ saturation at -1.0V and below.

References:

[1] Ishihara S., Okachi T., Naito H., Impedance spectroscopy measurements of charge carrier mobility in 4,4'-N,N'-dicarbazole-biphenyl thin films doped with tris(2-phenylpyridine) iridium Thin Solid Films, 2009, 518, 452–456.

[2] Rhee H.-W., Sik Chin K., Young Oh S., Choi J.-W., Application of impedance technique to OLED Thin Solid Films, 2000, 363, 236–239.

[3] del Pozo G., Arredondo B., Romero B., Susanna G., Brunetti F., Degradation of PEIE interlayer in PTB7:[70]PCBM based solar cells characterized by impedance spectroscopy Sol. Energy, 2017, 144, 105–110.