

## SUPPLEMENTARY MATERIAL FOR

### Polarization of Charge-Transfer Bands and Rectification in Hexadecylquinolinium 7,7,8-Tricyanoquinodimethanide and Its Tetrafluoro Analog

Andrei Honciuc [a], Akihiro Otsuka [b,c], Yu-Hsiang Wang [a], Samuel K. McElwee [a], Stephen A. Woski [a], Gunzi Saito [c], and Robert M. Metzger [a]\*

[a] Laboratory for Molecular Electronics, Chemistry Department, University of Alabama, Tuscaloosa, AL 35487-0336, USA.

[b] Research Center for Low-Temperature and Materials Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

[c] Division of Chemistry, Graduate School of Science, Kyoto University, Kita-Shirakawa, Oiwake-cho, Sakyo-ku, Kyoto 606-8502, Japan

\* Corresponding author. E-mail: rmetzger@bama.ua.edu

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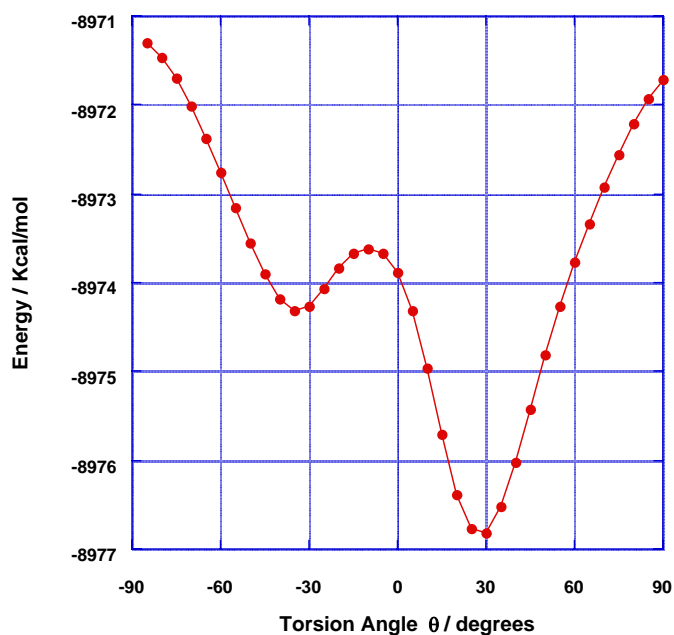
#### Synthesis

The synthesis of **5** [15] was improved here by using a two-fold excess of  $\text{Li}^+\text{TCNQF}_4^{\bullet-}$ , as was suggested for **1** [4]. All the solvents were distilled prior to use. Compound **5** was synthesized from the reaction of *N*-(hexadecyl)lepidinium bromide (0.503 g, 1.12 mmol) and  $\text{Li}^+\text{TCNQF}_4^{\bullet-}$  (0.633 g, 2.24 mmol) in dry DMSO (6 mL) in the presence of pyridine (0.35 mL). The above deep green mixture was heated at 105–110°C for 5 h under nitrogen atmosphere. The dark wine-red reaction mixture was cooled, and 25 mL of  $\text{CH}_3\text{CN}$  was added, then stored overnight in a refrigerator at 5°C. The resulting precipitate was filtered off, washed with chilled  $\text{CH}_3\text{CN}$  (25 mL), pure water (2 mL  $\times$  2), methanol (5 mL), and finally with hot methanol (50 mL), then dried *in vacuo* to separate compound **5** as a purple fine powder (0.411 g, 59.6% yield). MALDI-MS (*m/z*, % relative intensity): 617 ( $[\text{M}+\text{H}]^+$ , 100), 597 (42), 553 (16), 550 (21).  $^1\text{H}$ -NMR (DMSO-*d*<sub>6</sub>)  $\delta$  9.65 (d, 1H, *J* = 5.99 Hz), 8.51–8.68 (m, 4H), 8.32 (t, 1H, *J* = 7.99 Hz), 8.08–8.13 (m, 1H), 5.01–5.09 (m, 2H), 1.93–2.00 (m, 2H), 1.40 (broad s, 2H), 1.22 (m, 24H), 0.85 (t, 3H, *J* = 6.59 Hz).  $^{19}\text{F}$ -NMR (DMSO-*d*<sub>6</sub>) (353 K)  $\delta$  -146.48 (d, *J* = 13.91 Hz), -148.95 (d, *J* = 13.91 Hz). Anal. Found: C, 72.13; H, 6.56; N, 9.05; F, 12.43; Br, 0.00%. Calcd for  $\text{C}_{37}\text{H}_{40}\text{N}_4\text{F}_4$ : C, 72.04; H, 6.54; N, 9.09; F, 12.33; Br, 0.00%. Compound **6** was similarly synthesized from *N*-[(12-mercaptoacetyl)dodecane]lepidinium iodide (0.445 g, 0.867 mmol) and  $\text{Li}^+\text{TCNQF}_4^{\bullet-}$  (0.494 mg, 1.75 mmol) in dry DMSO (4.5 mL) in the presence of pyridine (0.27 mL) at around 100°C for 4 h under nitrogen atmosphere. The dark purple reaction mixture was cooled, and 25 mL of  $\text{CH}_3\text{CN}$  and 10 mL of  $(\text{Et})_2\text{O}$  were added, then the solution was stored in a refrigerator at 5°C. The resultant purple precipitate was filtered off, washed with  $\text{CH}_3\text{CN}$  (25 mL), pure water (2 mL  $\times$  2), methanol (10 mL), and finally with hot methanol (50 mL), then dried *in vacuo* to separate compound **6** as a purple powder (0.267 g, 48.5%). MALDI-MS (*m/z*, % relative intensity): 635 ( $[\text{M}+\text{H}]^+$ , 100), 427 (12), 387 (64).  $^1\text{H}$ -NMR (DMSO-*d*<sub>6</sub>)  $\delta$  9.66 (d, 1H, *J* = 5.84 Hz), 8.51–8.70 (m, 4H), 8.33 (t, 1H, *J* = 7.66 Hz), 8.09–8.14 (m, 1H), 5.02–5.09 (m, 2H), 2.80 (t, 2H, *J* = 7.19 Hz), 2.31 (s, 3H), 1.94–2.03 (m, 2H), 1.43–1.50 (m, 2H), 1.21–1.28 (m, 16H). Anal. Found: C, 66.53; H, 5.49; N, 8.74; S, 4.74%. Calcd for  $\text{C}_{35}\text{H}_{34}\text{N}_4\text{OSF}_4$ : C, 66.22; H, 5.40; N, 8.83; F, 11.98; S,

5.04%. From additional doublet peaks in NMR (not listed above), both **5** and **6** seem to have a minor (presumed) rotamer and/or aggregates at room temperature, and even at higher temperatures (up to 373 K) in DMSO- $d_6$ .

### Theoretical calculations

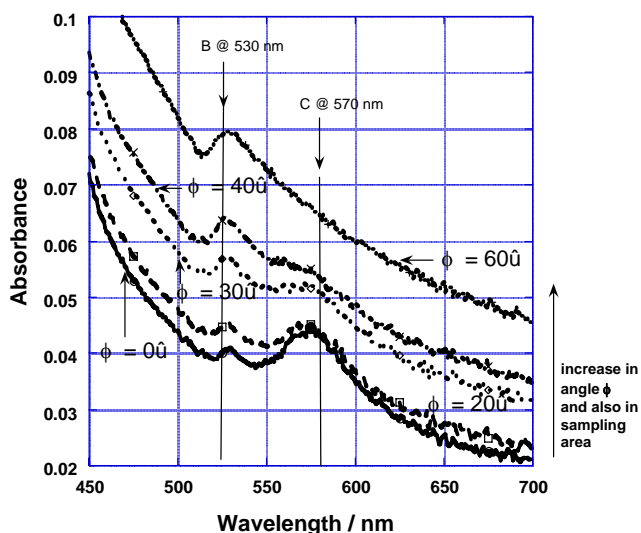
The heats of formation of a methyl analog of **5**, computed by semi-empirical molecular orbital theory PM3 as a function of the torsion angle  $\theta$  (illustrated in structure **1** of Fig. 1) yields (**Fig. A**) a global minimum (-8976.8 kcal/mol) at  $\theta = +25$  to  $+30^\circ$ , a local maximum of -8973.6 kcal/mol at  $\theta = -10^\circ$ , and a local minimum (-8974.3 kcal/mol) at  $\theta = -30$  to  $-35^\circ$ .



**Figure A.** Computed heats of formation of a methyl analog of **5**, as a function of the torsion angle  $\theta$  between the 3CNQF<sub>4</sub> plane and the quinolinium plane, calculated at the PM3 level.

### UV-Visible spectra of a mixed monolayer

We also studied a mixed multilayer. In **Figure B** we present the UV-Vis spectrum of a 14-layer film of **1** deposited on quartz, with the first 7 or so layers transferred below the collapse point at  $28 \text{ mN m}^{-1}$ , and the rest transferred at  $35 \text{ mN m}^{-1}$  (beyond the collapse point). The polarization dependence of bands B and C on the angle  $\phi$  is clearly seen, although the band maxima are slightly displaced from those of **Figure 6**.

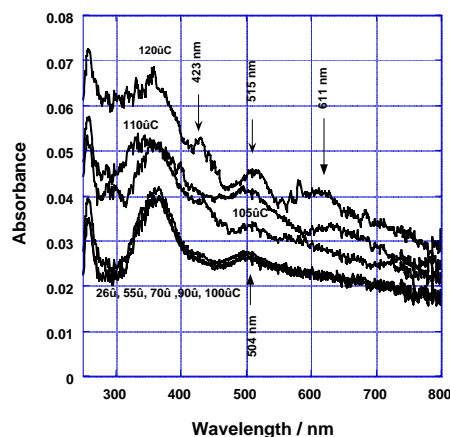


**Figure B.** Polarized UV-Vis spectra of 14 LB monolayers of **1**, deposited (the first 7 layers or so) at  $28 \text{ mN m}^{-1}$  and (the rest) at  $35 \text{ mN m}^{-1}$  onto the same quartz substrate. The baseline increases with angle  $\phi$  because the sampled area increases. The spectra clearly show the opposite polarization dependence of bands B and C.

If the spectra of **Figure B** are re-measured after several days, the angular dependence (polarization) is lost; a thermodynamically more favorable arrangement is probably reached.

### Temperature dependence of UV-Vis spectra of **5**

Unpolarized UV-Vis spectra of LB multilayers of **5** as a function of temperature are shown in **Figure C**. A shoulder at 423 nm sharpens by 120°C. A peak centered at 611 nm, invisible at 26°C, grows to a broad band at 120°C. Using the method used in [15], we obtained a Z-type 12-layer multilayer of **5** by alternate-layer deposition, but its UV-Vis spectrum at room temperature is identical to that of **Figure C**. The data reported for **5** in Ref. [15] may be due either to micelle formation, or to some artifact



**Figure C.** Unpolarized UV-Vis spectrum of a 12-layer Y-type 2-sided LB film of **5** on quartz (6 LB monolayers per side), as a function of temperature. A shoulder at 423 nm becomes distinct at 120°C. A second, more prominent, peak shifts from 504 nm at 26°C to 515 nm at 120°C. A band, invisible at 26°C, grows to a broad but weak band, centered at 611 nm at 120°C.