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Amidinium–carboxylate salt bridge mediated proton-coupled electron transfer in a donor-acceptor supramolecular system

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Materials and Instruments

All chemicals and solvents were purchased commercially and used without further purification. Diiodideterthiophene **1** and dibromo diketopyrrolopyrrole **4** were prepared according to literature reports.^{1,2}

All ¹H NMR and ¹³C NMR spectra were recorded on a JNM-ECZ400S/L 400MHz NMR spectrometer. Mass spectroscopic data were obtained at the South-Central University For Nationalities using an HP5973 mass spectrometer. UV-Vis spectra were recorded on a Shimadzu UV-2501PC UV-vis spectrophotometer. Fluorescence measurements were carried out on a Perkin-Elmer LS-55 spectrofluorophotometer using a xenon lamp as the light source. Excitation wavelengths of 390 and 600 mm were used. All UV and PL spectra were collected at room temperature. FT-IR spectra were recorded on a JASCO FT/IR-470 plus Fourier transform infrared spectrometer and measured as KBr pellets. Scanning electron microscopy (SEM) investigations were carried out on a HITACHI HT-7700 instrument. The samples for SEM tests were prepared by dropping a 1 mg mL⁻¹ sample as an NMP solution onto the surface of a silicon wafer and then evaporating off the NMP solvent under vacuum. Thermogravimetric analyses (TGA) were performed on a Perkin Elmer TGA 4000 instrument with the temperature increased from room temperature to 800 °C at a rate of 10 °C min⁻¹ under N₂. ITC titrations were performed using a MicroCal VP-ITC and were carried out in anhydrous NMP at 25 °C with the concentration of the 3T-Am and DPP-Ca subunits kept at 2 and 0.1 mM L⁻¹, respectively. After the titration was finished, the titration data was fitted to give the stoichiometry (n), the equilibrium association

constant (K_a), the apparent association enthalpy (Δ H) and entropy (Δ S). Cyclic voltammetry (CV) was performed at a scanning rate of 100 mV s⁻¹ on an AUTOLAB. PGSTAT30 potentiostat/ galvanostat system (Ecochemie, Netherlands), which was equipped with a three-electrode cell. The sample was dissolved in dichloromethane, and a glass carbon disk and Pt wire were used as the working electrode and counter electrode, respectively. An Ag/Ag⁺ couple was used as the reference electrode. Tetrabutylammonium hexafluorophosphate (n-Bu₄NPF₆, 0.1 mM) was used as the supporting electrolyte. Time-resolved emission studies were performed using an Edinburgh FL 920 photon counting system with a hydrogen-filled lamp as the excitation source.

¹H NMR spectral titrations. In 0.6 mL of the mixed solvent NMP:THF- d_8 (1:1, v:v), the monomer 3T-Am (1 mg, 2.939 × 10⁻³ mol L⁻¹) was kept at a fixed value (defined as one equivalent). With the DPP-Ca as the variable, the ¹H NMR spectrum was scanned 3000 times. As the amount of DPP-Ca was gradually increased from 0.75 mM to 1.5 mM, 2.25 mM, and 3 mM, the corresponding ¹H NMR spectrum was obtained.

¹H NMR spectral dilution studies. The supramolecular polymer 3T-DPP (3 mg, 2.993 $\times 10^{-3}$ mol L⁻¹) was dissolved in 0.6 mL of the mixed solvent NMP:THF-*d*₈ (1:1, v:v), and the ¹H NMR spectrum was scanned 3000 times. Under the same conditions, the volume of the mixed solvent system (NMP:THF-*d*₈, 1:1, v:v) was sequentially increased to 0.8, 1.2, and 2.4 mL, respectively, and the corresponding ¹H NMR spectrum was obtained.

UV-Vis absorption and fluorescence spectra. The UV-Vis absorption and fluorescence spectra were measured in NMP solvent at room temperature. Absorption and fluorescence spectra were determined at a monomer concentration of $10 \,\mu$ M (3 mL) in a 1 cm standard quartz cell. Excitation wavelengths were provided at 390 and 600 mm, respectively.

Transient emission spectroscopy. 3T-DPP , 3T-Am, and DPP-Ca were dissolved in NMP at a concentration of 1.0×10^{-5} mol L⁻¹ and used as the test solutions. The decay lifetime of the emission features of 3T-Am at 480 nm, DPP-Ca at 460 nm and 670 nm, and 3T-DPP at 480 nm and 670 nm were measured, respectively.

Synthesis

3,3''-Dioctyl-[2,2':5',2''-terthiophene]-5,5''-dicarbonitrile (2). Compound **1** (2 g, 2.76 mmol) and copper(I) cyanide(2.47 g, 27.6 mmol) were added in DMF (100 mL), and then the solution was stirred at 130 °C for 15 h. After cooling to room temperature, the solution was washed with aqueous ammonium hydroxide to remove residual copper(I) cyanide. The organic phase was extracted with dichloromethane and washed with brine. The organic layer was dried over anhydrous Na₂SO₄ and evaporated to dryness. The residue was purified by column chromatography on silica gel using dichloromethane/petroleum ether (v/v = 1/1) as the eluent to afford **2** (0.66 g, yield: 46%) as a yellow solid . ¹H NMR (400 MHz, CDCl₃) δ : 7.48 (s, 2H), 7.21 (s, 2H), 2.82-2.75 (m, 4H), 1.70-1.61 (m, 4H), 1.31 (br, 20H), 0.90 (t, *J* = 6.9 Hz, 6H). ¹³C NMR

(100 MHz, CDCl₃): δ 140.5, 139.9, 137.1, 135.3, 128.1, 114.1, 107.6, 31.8, 30.4, 29.4, 29.3, 29.2, 29.1, 22.7, 14.1.

Di-tert-butyl((3,3"-dioctyl-[2,2':5',2"-terthiophene]-5,5"-

diyl)bis(iminomethylene))dicarbamate (3). To a solution of 2 (2 g, 3.82 mmol) in THF (100 mL) was added lithium bis(trimethylsily)amide (3.2 g, 19.1 mmol) under N₂. The reaction mixture was stirred at room temperature overnight. After being acidified by adding 1 M HCl, the mixture was further stirred for two hours, and the mixture was concentrated to about 5 mL, then diluted by 100 mL THF. Aqueous sodium hydroxide (1.5 g, 38.2 mmol) and di-tert-butyl dicarbonate (4.23 g, 19.1 mmol) were added to the previous THF solution dropwise. The reaction mixture was then stirred at room temperature for 24 h. The organic phase was extracted with dichloromethane, washed with brine, and dried over anhydrous Na₂SO₄. After the solvent was evaporated, the crude product was purified by column chromatography on a silica gel using a mixture of ethyl acetate/petroleum ether (v/v = 1/4) as the eluent to afford **3** (2.2 g, yield: 76%) as a vellow solid. ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.96 (br, 4H), 7.90 (s, 2H), 7.31 (s, 2H), 2.79-2.64 (m, 4H), 1.68-1.52 (m, 4H), 1.40 (s, 18H), 1.25 (br, 20H), 0.79 (s, 6H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 163.5, 160.9, 140.4, 137.5, 135.8, 135.3, 132.8, 128.0, 78.3, 55.4, 31.8, 30.1, 29.5, 29.4, 29.3, 29.2, 28.4, 22.6, 14.4.

3,3''-Dioctyl-[2,2':5',2''-terthiophene]-5,5''-bis(carboximidamide) (**3T-Am).** Compound **3** (0.22 g, 0.291 mmol) was dissolved in trifuoroacetic acid (TFA) (10 mL). The reaction mixture was stirred at 0 °C overnight. The solution was evaporated to dryness under reduced pressure and the residue was re-dissolved in water under conditions of ultrasonification. 2 M NaOH aqueous solution was added leading a yellow solid to separate out. The solid was filtered, washed with water, dried in vacuum at 40 °C to give compound **3T-Am** (0.134 g, yield: 83%) as a yellow solid. ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.42 (s, 2H), 7.17 (s, 2H), 6.33 (s, 6H), 2.70-2.64 (m, 4H), 1.60-1.53 (m, 4H), 1.26-1.15 (m, 20H), 0.78 (d, *J* = 7.1 Hz, 6H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 157.2, 139.8, 139.3, 135.8, 132.4, 130.4, 127.4, 31.8, 30.4, 29.5, 29.4, 29.3, 29.2, 22.6, 14.5. MS (ESI): m/z (M⁺) calcd for C₃₀H₄₄N₄S₃, 556.8900; found, 557.5.

Di-tert-butyl5',5'''-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-

tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis([2,2'-bithiophene]-5-carboxylate) (5).

A mixture of compound **5** (2.04 g, 2 mmol), *tert*-butyl thiophene-2-carboxylate (0.92 g, 5 mmol), anhydrous K₂CO₃ (0.69 g, 5 mmol), pivalic acid (0.06 g, 0.6 mmol), and catalytic amount of palladium(II) acetate and anhydrous DMF (25 mL) were stirred under N₂ at 100 °C for 14 h. After cooling to room temperature, the reaction mixture was poured into water, extracted into dichloromethane, washed with brine. The organic layer was dried over anhydrous Na₂SO₄, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on a silica gel using a mixture of dichloromethane/petroleum ether (v/v = 1/1) as eluent to afford **6** (1.1 g, yield: 45%) as a dark blue solid. ¹H NMR (400 MHz, CDCl₃): δ 8.88 (d, *J* = 4.2 Hz, 2H), 7.64 (d, *J* = 3.9 Hz, 2H), 7.38 (d, *J* = 4.2 Hz, 2H), 7.23 (d, *J* = 3.9 Hz, 2H), 4.02 (d, *J* = 7.7 Hz, 4H), 1.93 (br, 4H), 1.58 (s, 18H), 1.19 (br, 64H), 0.85-0.82 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 161.6, 161.0, 141.7, 141.6, 139.5, 136.58, 135.4,

133.6, 129.4, 126.0, 125.1, 108.9, 82.3, 46.3, 37.9, 32.0, 31.5, 31.3, 30.2, 30.1, 29.72, 29.69, 29.8, 29.63, 29.58, 29.4, 29.3, 28.2, 26.3, 22.72, 22.70, 14.2.

5',5'''-(2,5-Bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-

1,4-diyl)bis(([2,2'-bithiophene]-5-carboxylic acid)) (DPP-Ca). TFA (10 mL) was slowly added to a solution of **6** (0.2 g, 0.163 mmol) in chloroform (10 mL) in an ice bath, and the mixture was stirred at room temperature overnight. The reaction solution was evaporated to dryness under reduced pressure and the residue was re-dissolved in THF. The solution was gradually added into petroleum ether, and then a dark purple solid precipitated. The solid was filtered, washed with dichloromethane, dried in vacuum at 40 °C to give the compound **DPP-Ca** (0.156 g, yield: 86%) as a dark purple solid. ¹H NMR (400 MHz, THF-*d*₈): δ 9.05 (s, 2H), 7.61 (s, 2H), 7.52 (s, 2H), 7.37 (s, 2H), 4.05 (s, 2H), 1.99 (s, 4H), 1.26 (s, 64H), 0.83 (s, 12H). ¹³C NMR (100 MHz, THF-*d*₈): δ 161.0, 141.7, 141.2, 138.9, 136.6, 129.3, 125.7, 125.3, 108.7, 100.0, 70.4, 32.0, 31.9, 30.1, 29.79, 29.78, 29.73, 29.71, 29.69, 29.68, 29.64, 29.59, 29.43, 29.38, 26.71, 26.2, 22.6, 13.6. MS (ESI): m/z (M⁺) calcd for C₆₄H₉₂N₂O₆S₄, 1113.6880; found, 1113.1.

Synthesis of polymers (3T-DPP). Compound 3T-Am (100 mg, 0.180 mmol), compound DPP-Ca (167 mg, 0.180 mmol) were dissolved in THF (20 mL). The solution was stirred at room temperature 10 minutes, and then a black solid precipitated. The solid was filtered, washed with THF, dried in vacuum at 40 °C to give the **3T-DPP** (0.248 mg, yield: 93%) as a black solid. ¹H NMR (400 MHz, NMP:THF- d_8 , 1:1 (v:v)): δ 11.75 (s, 2H), 9.07 (s, 2H), 8.97 (s, 2H), 8.18 (s, 2H), 7.64 (s, 2H), 7.51-7.43 (m, 6H).

The product showed poor solubility in common NMR solvents and this precluded recording a ¹³C NMR spectrum. Unfortunately, the supramolecular system 3T-DPP showed only moderate solubility in NMP, poor solubility in CHCl₃, THF, and DMF, and essentially no solubility in hexanes, dichloromethane, ethyl acetate, acetone, diethyl ether, acetonitrile, toluene, 1,2-dichloroethane, and 1,4-dioxane.

NMR and MS spectra



Figure S1. ¹H NMR spectrum of **3T-Am** in DMSO- d_6 .



Figure S2. ¹³C NMR spectrum of 3T-Am in DMSO- d_6 .



Figure S3. MS spectrum of 3T-Am.



Figure S4. ¹H NMR spectrum of DPP-Ca in THF- d_8 .



Figure S5. ¹³C NMR spectrum of **DPP-Ca** in THF- d_8 .



Figure S6. MS spectrum of DPP-Ca.



Figure S7. ¹H NMR spectrum of 3T-DPP in NMP:THF- d_8 , 1:1 (v:v).



Figure S8. Stacked partial ¹H NMR spectra (400 Hz, NMP:THF- d_8 , 1:1 (v:v) , 298 K) of (a) DPP-Ca, (b) 3T-Am, and 3 mM 3T-Am recorded upon the addition of 0.75 mM (c), 1.5 mM (d), 2.25 mM (e), and 3 mM (f) of DPP-Ca.



Figure S9. Stacked partial ¹H NMR spectra (400 MHz, NMP:THF- d_8 , 1/1 (v/v), 298 k) of solutions of 3T-DPP at different concentrations: (a) 3 mM, (b) 2.25 mM, (c) 1.5 mM,

(d) 0.75 mM.



Figure S10. TGA curves of DPP-Ca and 3T-DPP recorded under a nitrogen atmosphere at the heating rate of 10 $^{\circ}$ C min⁻¹.



Figure S11. The supramolecular polymer may be reversibly "broken up" and "reformed" by adjusting pH value of the DMSO solution.



Figure S12. Determination of the oxidation potential of the model compound 3,3"dioctyl-2,2':5',2"-terthiophene in dichloromethane/0.1 M Bu₄NPF₆ at a scan rate of 100 mV s⁻¹. $E(D^+/D) = 0.45$ eV.

Ab Initio Calculations

DFT calculations were performed using the numeric atom-centred basis set allelectron code FHI-AIMS.^{3,4} Tight basis sets were used with tier 2 basis functions for all species. Electronic exchange and correlation were modelled with the B3LYP exchange-correlation functional. To treat spin orbit coupling, the atomic zeroth-order regular approximation (ZORA)1 was used. Van der Waals forces were accounted for by applying a Tkatchenko-Sheffler electrodynamic screening scheme.⁵ Structures were relaxed with a convergence criteria of 10^{-4} eV Å⁻¹ for forces, 10^{-5} electrons for the electron density, and 10^{-6} eV for the total energy. These settings ensured highly converged energies and equilibrium distances.



Figure S13. Energy-optimized structure of the repeating unit within supramolecular polymer 3T-DPP.

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