

## Electronic Supplementary Information

### Photochromism of a diarylethene charge-transfer complex: photochemical control of intermolecular charge-transfer interaction

Masakazu Morimoto,<sup>a</sup> Seiya Kobatake<sup>b</sup> and Masahiro Irie<sup>a\*</sup>

<sup>a</sup> *Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan*

<sup>b</sup> *Department of Applied and Bioapplied Chemistry, Graduate School of Engineering, Osaka City University, Sugimoto 3-3-138, Sumiyoshi-ku, Osaka 558-8585, Japan*

## Contents

1. Materials and Instrumentation
2. Syntheses
3. Cyclic voltammograms of 1, TMPD, and TCNQF<sub>4</sub>
4. Molecular orbital calculations
5. Absorption spectrum of K<sup>+</sup>TCNQF<sub>4</sub><sup>-</sup>
6. Absorption spectral change of 1a under bulk electrolysis
7. Determination of stoichiometric ratio of EDA complexes (Job-plot analysis)
8. Determination of binding constants of EDA complexes

## 1. Materials and Instrumentation

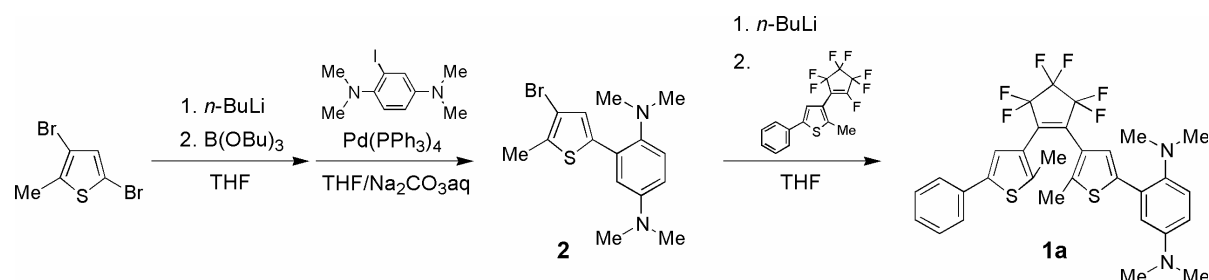
Solvents used were spectroscopic grade and purified by distillation before use. 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyano-*p*-quinodimethane (TCNQF<sub>4</sub>) and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) were purchased from Tokyo Kasei Kogyo Co., Ltd. and Wako Pure Chemical Industries, Ltd., respectively, and were purified by recrystallization from acetonitrile before use.

<sup>1</sup>H NMR spectra were recorded with a Bruker Avance 400 spectrometer (400 MHz). Tetramethylsilane (Me<sub>4</sub>Si) was used as an internal standard. Mass spectra were recorded with a Shimadzu GCMS-QP5050A gaschromatography-mass spectrometer. Elemental analyses were carried out at the Service Centre of Elemental Analysis of Kyushu University.

Absorption spectra in solution were measured with a Hitachi U-3410 absorption spectrophotometer. Photoirradiation was carried out using an Ushio 500 W super high-pressure mercury lamp. Monochromic light was obtained by passing the light through a monochromator (Ritsu MV-10N).

Cyclic voltammetry was performed on an ALS CHI600A electrochemical analyser. A three-electrode assembly (Bioanalytical Systems (BAS)) was used, which was equipped with a platinum working electrode, a platinum wire as the counter electrode, and Ag/Ag<sup>+</sup> (tetra-*n*-butylammoniumperchlorate (TBAP)/acetonitrile) electrode as the reference electrode. The scan rate was 0.1 V s<sup>-1</sup>. The bulk electrolysis was performed on a BAS CV-50W electrochemical analyser. A quartz cell (1 × 10 × 30 mm; BAS) was used, which was equipped with a platinum working electrode, a platinum mesh as the counter electrode, and Ag/Ag<sup>+</sup> (TBAP/acetonitrile) electrode as the reference electrode. Absorption spectra under the bulk electrolysis were measured with an Ocean Optics S2000 spectrometer. Sample solutions for the electrochemical analyses were prepared by dissolving compounds in acetonitrile containing TBAP (0.1 mol dm<sup>-3</sup>) as a supporting electrolyte, and were degassed through an argon stream.

## 2. Syntheses



### 2-1. 2-(4-Bromo-5-methyl-2-thienyl)-*N,N,N',N'*-tetramethylbenzene-1,4-diamine (**2**)

To a dry THF solution (20 cm<sup>3</sup>) containing 3,5-dibromo-2-methylthiophene (1.9 g, 7.4 mmol) was added 15% *n*-BuLi hexane solution (4.7 cm<sup>3</sup>, 7.7 mmol) at -78 °C under argon atmosphere, and the reaction mixture was stirred for 2 h at the low temperature. Tri-*n*-butylborate (3.0 cm<sup>3</sup>, 11 mmol) was slowly added to the reaction mixture at -78 °C, and the mixture was stirred for 3 h at the temperature. A small amount of water was added to the mixture. To the reaction mixture were added 20 wt% Na<sub>2</sub>CO<sub>3</sub>aq (15 cm<sup>3</sup>), 2-iodo-*N,N,N',N'*-tetramethylbenzene-1,4-diamine<sup>S1</sup> (2.0 g, 5.9 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (240 mg, 0.21 mmol). The mixture was refluxed for 14 h at 75 °C. The mixture was neutralized with 2.0 mol dm<sup>-3</sup> HCl, and then extracted with diethyl ether. The organic layer was dried over MgSO<sub>4</sub>, filtrated, and concentrated. The residue was chromatographed on alumina with hexane to give **2** (690 mg, 28%) as pale yellow crystals (Found: C, 53.26; H, 5.64; N, 8.29. C<sub>15</sub>H<sub>19</sub>BrN<sub>2</sub>S requires C, 53.10; H, 5.64; N, 8.26%); δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 2.39 (3 H, s, Me), 2.58 (6 H, s, 2 × Me), 2.94 (6 H, s, 2 × Me), 6.68 (1 H, dd, *J*2.8 and 8.4, Ph), 6.92 (1 H, d, *J*2.8, Ph), 7.12 (1 H, d, *J*8.4, Ph) and 7.24 (1 H, s, thienyl); *m/z* (EI) 338 and 340 (M<sup>+</sup>).

### 2-2. 1-[5-(1,4-dimethylamino-2-phenyl)-2-methyl-3-thienyl]-2-(2-methyl-5-phenyl-3-thienyl)-perfluorocyclopentene (**1a**)

To a dry THF solution (6 cm<sup>3</sup>) containing **2** (320 mg, 0.94 mmol) was added 15% *n*-BuLi hexane solution (0.60 cm<sup>3</sup>, 0.98 mmol) at -78 °C under argon atmosphere, and the reaction mixture was stirred for 2 h at the low temperature. A dry THF solution (2 cm<sup>3</sup>) of 3-(2,3,3,4,4,5,5-heptafluorocyclopent-1-en-1-yl)-2-methyl-5-phenylthiophene<sup>S2</sup> (350 mg, 0.96

mmol) was slowly added to the reaction mixture at  $-78\text{ }^{\circ}\text{C}$ , and the mixture was stirred for 6 h at the temperature. The reaction was stopped by the addition of water. The mixture was neutralized with  $2.0\text{ mol dm}^{-3}$  HCl, and then extracted with diethyl ether. The organic layer was dried over  $\text{MgSO}_4$ , filtrated, and concentrated. The residue was chromatographed on alumina with hexane to give **1a** (100 mg, 17%) as pale yellow crystals (Found: C, 61.33; H, 4.71; N, 4.68.  $\text{C}_{31}\text{H}_{28}\text{F}_6\text{N}_2\text{S}_2$  requires C, 61.37; H, 4.65; N, 4.62%).  $\delta_{\text{H}}$ (400 MHz; [D6]acetone;  $\text{Me}_4\text{Si}$ ) 2.09 (3 H, s, Me), 2.11 (3 H, s, Me), 2.54 (6 H, s,  $2 \times \text{Me}$ ), 2.87 (6 H, s,  $2 \times \text{Me}$ ), 6.73 (1 H, dd,  $J$  2.8 and 8.8, Ph), 6.95 (1 H, d,  $J$  2.8, Ph), 7.18 (1 H, d,  $J$  8.8, Ph), 7.32–7.67 (5 H, m, Ph), 7.49 (1 H, s, thienyl) and 7.51 (1 H, s, thienyl);  $m/z$  (EI) 606 ( $\text{M}^+$ );  $\lambda_{\text{max}}$ (acetonitrile)/nm 274 ( $\epsilon/\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$  44 800).

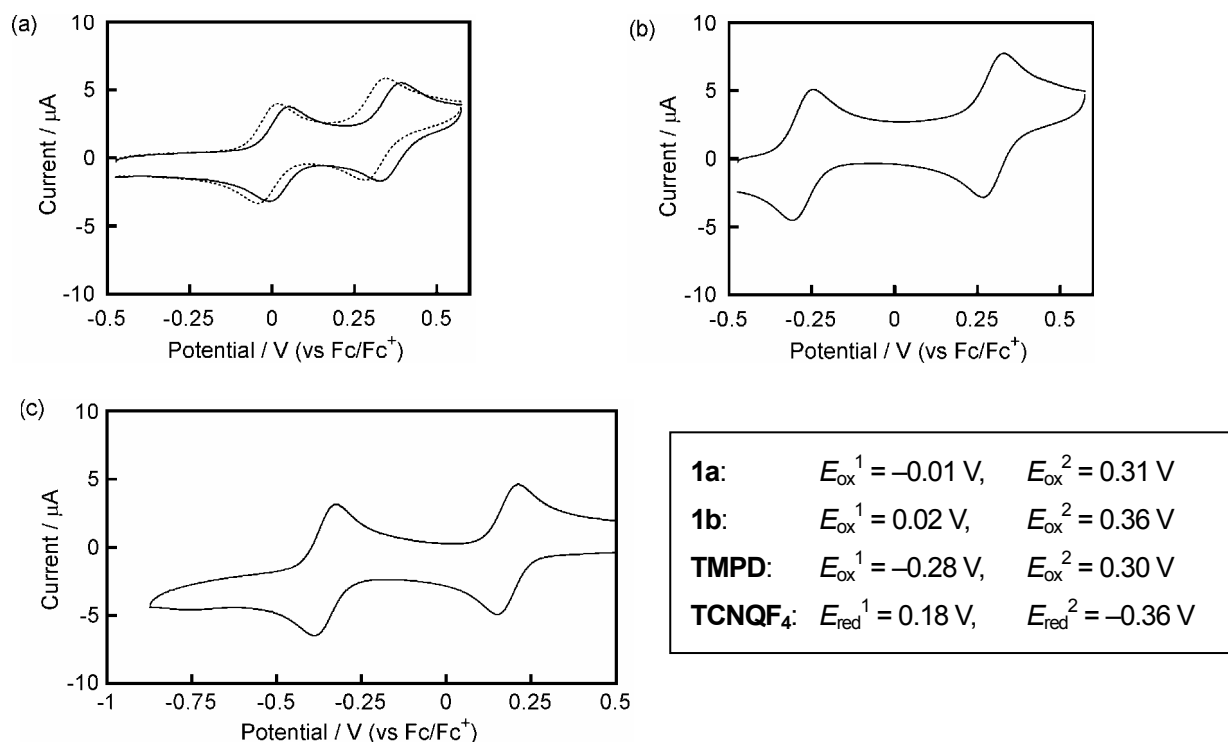
### 2-3. Closed-ring isomer of **1a** (**1b**)

**1b** was isolated by passing a photostationary solution containing **1a** and **1b** through a HPLC (Hitachi L-7100 pump system equipped with Hitachi L-7400 detector, Kanto Chemical reversed-phase column RP-18(H), acetonitrile as the eluent). Retention times for **1a** and **1b** were 48 and 54 min, respectively. **1b** was obtained as dark blue crystals (Found: C, 61.31; H, 4.75; N, 4.59.  $\text{C}_{31}\text{H}_{28}\text{F}_6\text{N}_2\text{S}_2$  requires C, 61.37; H, 4.65; N, 4.62%).  $\delta_{\text{H}}$ (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 2.10 (3 H, s, Me), 2.22 (3 H, s, Me), 2.64 (6 H, s,  $2 \times \text{Me}$ ), 2.95 (6 H, s,  $2 \times \text{Me}$ ), 6.68 (1 H, s, olefinic), 6.75 (1 H, s, olefinic), 6.81 (1 H, d,  $J$  8.0, Ph), 6.86 (1 H, s, Ph), 7.08 (1 H, d,  $J$  8.0, Ph) and 7.40–7.59 (5 H, m, Ph);  $m/z$  (EI) 606 ( $\text{M}^+$ );  $\lambda_{\text{max}}$ (acetonitrile)/nm 273 ( $\epsilon/\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$  25 600), 306 (26 400), 380 (11 200) and 600 (17 800).

### 2-4. Potassium salt of TCNQF<sub>4</sub> ( $\text{K}^+\text{TCNQF}_4^-$ )

$\text{K}^+\text{TCNQF}_4^-$  was prepared by the method of Melby et al.<sup>S3</sup> Found: C, 45.71; H, 0.00; N, 17.79.  $\text{C}_{12}\text{F}_4\text{KN}_4$  requires C, 45.72; H, 0.00; N, 17.77%.

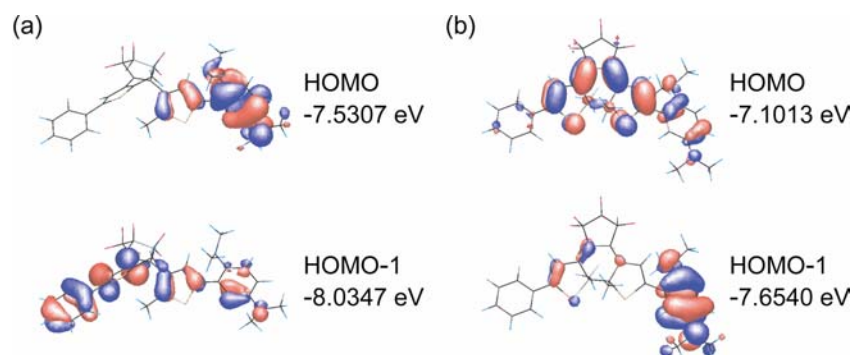
### 3. Cyclic voltammograms of **1**, TMPD, and TCNQF<sub>4</sub>



**Fig. S1** Cyclic voltammograms of (a) **1a** (dotted line,  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>) and **1b** (solid line,  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>), (b) **TMPD** ( $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>), and (c) **TCNQF<sub>4</sub>** ( $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>) in acetonitrile containing 0.1 mol dm<sup>-3</sup> TBAP (vs ferrocene/ferrocene<sup>+</sup>). Scan rate was 0.1 V s<sup>-1</sup>.

### 4. Molecular orbital calculations

Preliminary calculations of molecular geometry optimization were computed with the MM2 method (CS Chem3D Ultra program).<sup>S4</sup> After that, main calculations were computed with the Hartree-Fock (HF) functional and the 6-31G\* basis set (Gaussian 03 program).<sup>S5</sup>



**Fig. S2** Optimized structures of (a) **1a** and (b) **1b** with HOMO orbitals calculated by HF/6-31G\*.

## 5. Absorption spectrum of $\text{K}^+\text{TCNQF}_4^-$

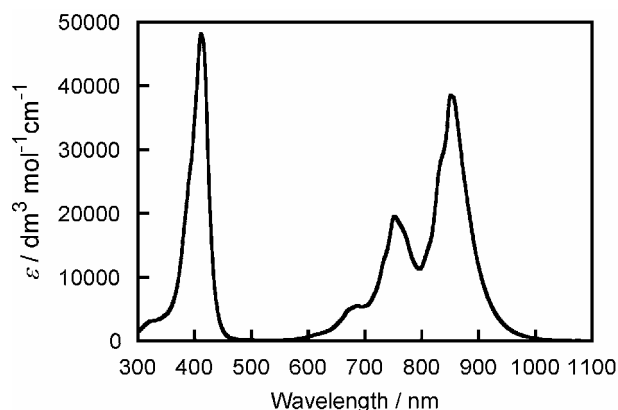


Fig. S3 Absorption spectrum of  $\text{K}^+\text{TCNQF}_4^-$  in acetonitrile.

## 6. Absorption spectral change of **1a** under bulk electrolysis

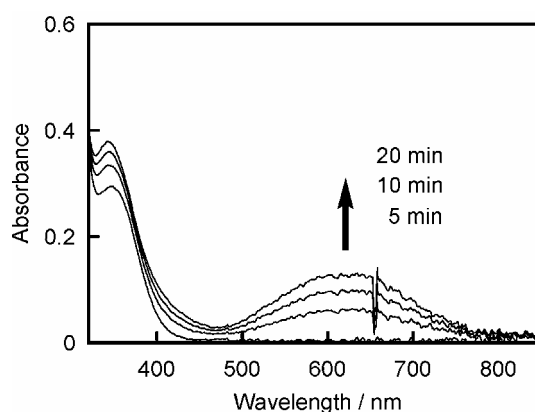


Fig. S4 Absorption spectral change of **1a** under bulk electrolysis in acetonitrile containing  $0.1 \text{ mol dm}^{-3}$  TBAP.

The potential was set at  $+0.2 \text{ V}$  (vs  $\text{Ag}/\text{Ag}^+$ ) where the first oxidation of **1a** occurs.

## 7. Determination of stoichiometric ratio of EDA complexes (Job-plot analysis)<sup>S6</sup>

Solutions of **1a**, **1b**, and  $\text{TCNQF}_4$  ( $1.00 \times 10^{-4} \text{ mol dm}^{-3}$ , a mixed solvent of chloroform and acetonitrile (v/v 10:1)) were prepared. The solutions of the donors (**1a** or **1b**) and the acceptor ( $\text{TCNQF}_4$ ) were mixed in various ratios with keeping the total volume as  $4 \text{ cm}^3$ , and absorption spectra of the mixed solutions were measured. The absorbance at 550, 863, and 1300 nm (550 nm:  $\mathbf{1a}^+$ , 863 nm:  $\text{TCNQF}_4^-$ , 1300 nm: charge-transfer (CT) complexes  $\mathbf{1a}\cdot\text{TCNQF}_4$  and  $\mathbf{1b}\cdot\text{TCNQF}_4$ ) was plotted against the molar fraction of donor ( $\chi = [\text{donor}]/([\text{donor}] + [\text{acceptor}])$ ).

## 8. Determination of binding constants of EDA complexes<sup>S7</sup>

Binding constants between **1** and TCNQF<sub>4</sub> were determined based on the following equilibrium:



where **D**, **A**, **D·A**, **D<sup>•+</sup>**, and **A<sup>•-</sup>** are neutral donor (**1a** or **1b**), neutral acceptor (TCNQF<sub>4</sub>), CT complex (**1a·TCNQF<sub>4</sub>** or **1b·TCNQF<sub>4</sub>**), radical cation of donor (**1a<sup>•+</sup>** or **1b<sup>•+</sup>**), and radical anion of acceptor (TCNQF<sub>4<sup>•-</sup></sub>), respectively. The product of binding constants  $K_1$  and  $K_2$  ( $K_1K_2 = K$ ) is presented as follows:

$$K = K_1K_2 = ([D^+][A^-])/([D][A]) = ([D^+][A^-])/([D]_0 - [DA] - [D^+])([A]_0 - [DA] - [A^-]) \quad (1)$$

where  $[D]$ ,  $[A]$ ,  $[D^+]$ ,  $[A^-]$ ,  $[DA]$  are the concentration of neutral donor, neutral acceptor, radical cation of donor, radical anion of acceptor, and CT complex under the equilibrium, respectively, and  $[D]_0$  and  $[A]_0$  are the total concentration of donor and acceptor, respectively. Because  $[DA]$  is very small and negligible in the system herein, it can be eliminated in eq. (1) as follows:

$$K = ([D^+][A^-])/([D]_0 - [D^+])([A]_0 - [A^-]) \quad (2)$$

Because of the charge balance,  $[D^+] = [A^-]$ , eq. (2) is:

$$K = [A^-]^2/([D]_0 - [A^-])([A]_0 - [A^-]) \quad (3)$$

Eq. (3) can be rearranged as follows:

$$[A^-] = \left\{ K([D]_0 + [A]_0) - \sqrt{K^2([D]_0 + [A]_0)^2 - 4K(K-1)[D]_0[A]_0} \right\} / 2(K-1) \quad (4)$$

Based on the Lambert-Beer's law, the absorbance  $A$  for a solution with 1-cm light-path length is:

$$A = \varepsilon_A[A^-] = \varepsilon_A \left\{ K([D]_0 + [A]_0) - \sqrt{K^2([D]_0 + [A]_0)^2 - 4K(K-1)[D]_0[A]_0} \right\} / 2(K-1) \quad (5)$$

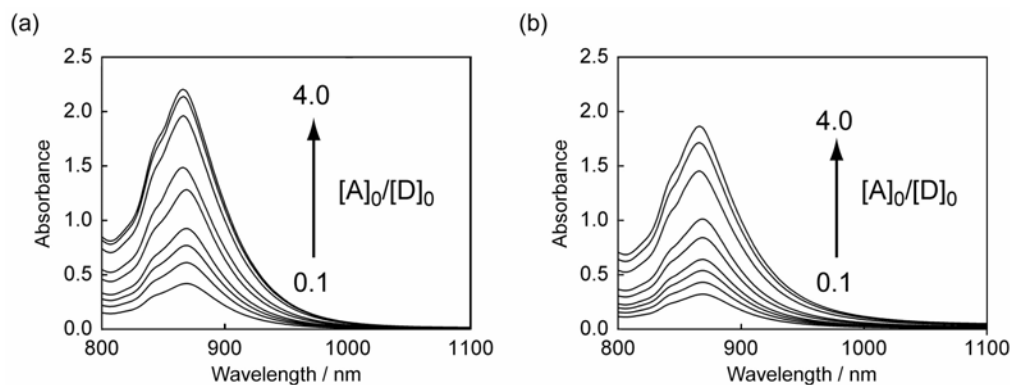
where  $\varepsilon_A$  is the extinction coefficient of radical anion of acceptor.

In the experiment, absorption spectra of the mixed solutions containing constant  $[D]_0$  and various  $[A]_0$  were measured. The experimental condition is as follows:

$$[D]_0 = 7.42 \times 10^{-5} \text{ mol dm}^{-3}, [A]_0/[D]_0 = 0.1-4.0, \text{ in } 1,1,2\text{-trichloroethane, } 1\text{-cm thick optical cell}$$

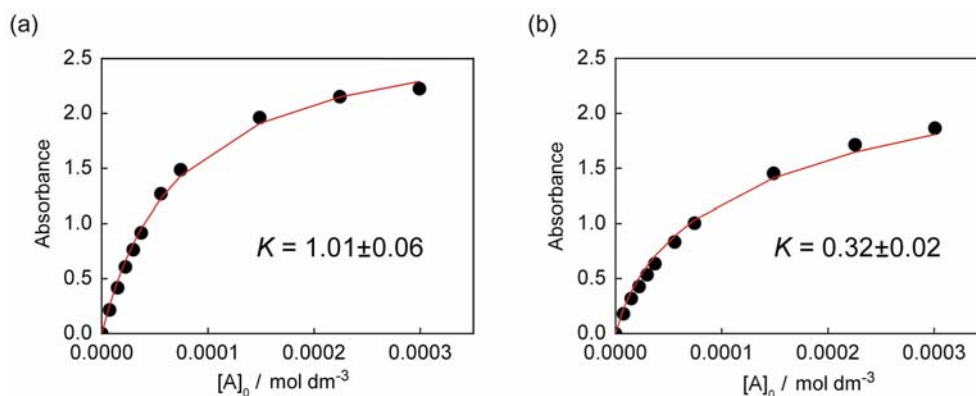
The absorption spectra are shown in Figure S5. The absorbance  $A$  of radical anion of acceptor (TCNQF<sub>4<sup>•-</sup></sub>) at 866 nm was plotted against  $[A]_0$  as shown in Figure S6.  $K$  values were determined by

the fitting of the plots on eq. (5), using Origin program.<sup>S8</sup> For  $\varepsilon_A$ , the extinction coefficient of  $K^+TCNQF_4^-$  (Figure S3) was used.



**Fig. S5** Absorption spectra of mixtures of (a) **1a** and  $TCNQF_4$  and (b) **1b** and  $TCNQF_4$  in 1,1,2-trichloroethane:

$[D]_0 = 7.42 \times 10^{-5} \text{ mol dm}^{-3}$ ;  $[A]_0/[D]_0 = 0.1-4.0$ .



**Fig. S6** Plots of absorbance of radical anion of  $TCNQF_4$  ( $TCNQF_4^-$ ) at 866 nm against  $[A]_0$  for mixtures of (a) **1a** and  $TCNQF_4$  and (b) **1b** and  $TCNQF_4$ .



## References

- S1 Y. Nakamura and H. Iwamura, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 3724–3728.
- S2 A. Peters, C. Vitols, R. MacDonald and N. R. Branda, *Org. Lett.*, 2003, **5**, 1183–1186.
- S3 L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson and W. E. Mochel, *J. Am. Chem. Soc.*, 1962, **84**, 3374–3387.
- S4 *CS Chem3D Ultra 6.0*, CambridgeSoft.Com, Cambridge MA.
- S5 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03 (Revision C.02)*, Gaussian, Inc., Wallingford CT, 2004.
- S6 K. A. Connors, *Binding Constants: The Measurement of Molecular Complex Stability*, Wiley-Interscience, New York, 1987, pp. 24–26.
- S7 R. Foster, *Organic Charge-Transfer Complexes*, Academic Press, London, 1969, pp. 125–178.
- S8 *Origin 6.1*, OriginLab Corp., Northampton MA.