

Electronic Supplementary Information for

Implementation of Redox Gradients in Hydrogen Bonded Complexes – Containing *N,N*-Dimethylaniline, Flavin and Fullerene Derivatives

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Synthetic procedure (S1)

5-Bromoisophthalic acid (1a). KMnO₄ (21.67 g, 0.14 mol) was added to a suspension of 1-bromo-3,5-xylene (12 g, 0.065 mol, 8.82 cm³) in *tert*-butanol/H₂O (1:1) (120 cm³). After heating the suspension for 1 h at 100 °C further KMnO₄ (21.67 g, 0.14 mol) was added. The suspension was heated at 100 °C for further 20 h and then cooled down to room temperature. After filtration over celite and washing with water, the filtrate was reduced to one-third and acidified with conc. HCl. The appearing white precipitate was dissolved in a conc. NaHCO₃ solution and washed three times with 100 cm³ diisopropylether. After further acidification with conc. HCl the white precipitate was collected and dried at 80 °C overnight. Yield: 12.70 g (80%). δ_{H} (400 MHz; DMSO-*d*₆; Me₄Si) 13.52 (broad s, 2H, COOH) 8.38 (s, 1H), 8.25 (s, 2H), 3.78 (broad s, COOH, 2H). δ_{C} (100.5 MHz; DMSO-*d*₆; Me₄Si) 165.35 (2C), 135.74 (2C), 133.49 (2C), 128.96 (1C), 122.03 (1C). EA: calculated for C₈H₅O₄Br (245.03): C 39.21; H 2.06; found: C 40.21, H 2.29. IR (diamond, RT): ν_{max} /cm⁻¹ 2990, 21360, 1698, 1449, 1399, 1275, 1266, 903, 753, 712.

5-Bromoisophthaloyl dichloride (2a). A solution of 5-bromoisophthalic acid (6.00 g, 24.49 mmol) in thionyl chloride (30 cm³) and *N,N'*-dimethylformamide (five drops) was refluxed for 6 h under dry conditions with subsequent vacuum distillation of the thionyl chloride excess. The residue was dried under high vacuum and yielded a red-brownish oil. Yield: 6.63 g (100%). δ_{H} (400 MHz; DMSO-*d*₆; Me₄Si) 8.36 (s, 1H), 8.19 (s, 2H). δ_{C} (100.5 MHz; DMSO-*d*₆; Me₄Si) 165.38 (2C), 135.78 (2C), 133.59 (2C), 128.92 (1C), 122.08 (1C).

***N,N'*-Bis[6-(3,3-dimethylbutyrylamino)pyridin-2-yl]-5-bromoisophthalamide (4a).** A solution of diacid dichloride **2a** (2.71 g, 9.61 mmol) in dry THF (40 cm³) was added dropwise to a solution of *N*-(6-aminopyridine-2-yl)-3,3-dimethylbutyramide **3** (4.35 g, 20.99 mmol) and triethylamine (2.70 cm³, 19.30 mmol) in dry THF (40 cm³) at 0° C. The solution was stirred at RT for 12 h, the residue filtered off, and the solvent removed under reduced pressure. Purification by column chromatography on silica gel (CH₂Cl₂/ethyl acetate (2:1) as eluent) gave a yellowish solid. Yield: 5.53 g (92%). δ_{H} (400 MHz; DMSO-*d*₆; Me₄Si) 9.76 (broad s, 2H, NH), 9.10 (broad s, 2H, NH), 8.46 (s, 1H), 8.29 (s, 2H), 8.01 (m, 4 H), 7.73 (d, ³*J* = 8.05 Hz, 2H), 2.27 (s, 4H), 1.08 (s, 18 H). δ_{C} (100.5 MHz; THF-*d*₈; Me₄Si) 170.80 (2C), 164.25 (2C), 151.70 (2C), 151.05 (2C), 140.56 (2C), 138.07 (2C), 134.36 (2C), 126.63 (1C), 123.09 (1C), 110.49 (2C), 110.20 (2C), 50.68 (2C), 31.63 (2C), 29.98 (6C). MS (FAB, NBA): *m/z* = 625 [M]⁺. Anal. calcd for C₃₀H₃₇O₅N₆Br•EtOAc (711.65): C 57.38, H 6.09, N 11.81; found: C 56.97, H 5.79, N 12.22. IR (diamond, RT): ν_{max} /cm⁻¹ 2955, 2361, 1684, 1671, 1558, 1541, 1521, 1508, 1446, 1298, 1277, 1241, 764, 750.

***N*-(6-(3,3-Dimethylbutanamido)pyridin-2-yl)3-iodobenzamide (5).** 4-Dimethylaminopyridine (DMAP) (247 mg, 2.02 mmol), 1-hydroxybenzotriazol (1-HOBT) (300 mg, 2.22 mmol) and 3-iodobenzoic acid (500 mg, 2.02 mmol) were dissolved in dry CH₂Cl₂ (50 cm³) and cooled to 0 °C. Then *N,N'*-dicyclohexylcarbodiimide (DCC) (584 mg, 2.83 mmol) was added and the reaction mixture stirred for 30 min at 0°C before *N*-(6-aminopyridin-2-yl)-3,3-dimethylbutanamide (520 mg,

2.52 mmol) was added at once. This mixture was stirred overnight and was allowed to reach room temperature. After filtration and evaporation of the solvent the crude product was cleaned by column chromatography on silica ($\text{CH}_2\text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2/\text{EtOAc}$ 4:1). Yield: 547 mg (62%). δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 8.15 (s, 1H), 8.12 (s, 1H, NH), 7.93 (m, 2H), 7.80 (m, 2H), 7.69 (t, $^3J = 8.01$ Hz, 1H), 7.51 (s, 1H, NH), 7.16 (t, $^3J = 8.12$ Hz, 1H), 2.18 (s, 2H), 1.04 (s, 9H). δ_{C} (100.5 MHz; CDCl_3 ; Me_4Si) 169.81 (1C), 163.34 (1C), 149.96 (1C), 149.61 (1C), 141.53 (1C), 141.37 (1C), 136.51 (1C), 130.89 (1C), 126.70 (2C), 110.31 (1C), 110.00 (1C), 94.87 (1C), 52.19 (1C), 31.77 (1C), 30.20 (3C). MS (FAB, NBA): $m/z = 438$ [M] $^+$. Anal. calcd for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}_3\text{I}$ (437.27): C 49.56, H 4.39, N 7.33; found: C 49.35, H 4.10, N 9.81. IR (diamond, RT): $\nu_{\text{max}}/\text{cm}^{-1}$ 2957, 1672, 1584, 1506, 1446, 1298, 1277, 1259, 1243, 798, 764, 749.

***N,N'*-Bis[6-(3,3-dimethylbutyrylamino)pyridin-2-yl]-5-((4-formylphenyl)ethynylisophthalamide (6).** After dissolving *N,N'*-bis(6-(3,3-dimethylbutan-amino)pyridin-2-yl)-5-iodoisophthalamide (iodo Hamilton Receptor: **4b**) (500 mg, 0.746 mmol) in dry THF (12 cm^3) and NEt_3 , (8 cm^3) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (6 mg, 0.0075 mmol) and CuI (4 mg, 0.022 mmol) were added. To dissolve the catalysts stirring at room temperature for 15 min is needed. Finally 4-ethynylbenzaldehyde (130 mg, 0.97 mmol) was added. The reaction mixture was stirred for 20 h, filtered and the solvent was removed in vacuum. Column chromatography of the residue (toluene/ 5% EtOH) was used to isolate the desired product. Yield: 520 mg (99 %). δ_{H} (400 MHz; $\text{DMSO}-d_6$; Me_4Si) 10.50 (broad s, 2H, NH), 10.05 (s, 1H), 9.81 (broad s, 2H, NH), 8.55 (s, 1H), 8.35 (d, $^3J = 6.61$, 2H), 7.98 (d, $^3J = 8.25$, 4H), 7.94 (m, 4H), 7.83 (d, $^3J = 7.97$ Hz, 2H), 2.32 (s, 4H), 1.03 (s, 18 H). δ_{C} (100.5 MHz; $\text{DMSO}-d_6$; Me_4Si) 192.00 (1C), 170.60 (2C), 164.15 (2C), 150.33 (2C), 149.79 (1C), 139.67 (2C), 138.83 (2C), 136.33 (2C), 132.93 (4C), 131.94 (2C), 129.32 (2C), 123.99 (1C), 110.36 (2C), 109.95 (2C), 82.18 (1C), 75.93 (1C), 54.52 (2C), 30.22 (2C), 29.33 (6C). MS (FAB, NBA): $m/z = 673$ [M] $^+$. FT-IR (diamond, RT): $\nu_{\text{max}}/\text{cm}^{-1}$ 3282, 2954, 2361, 1683, 1585, 1540, 1509, 1446, 1300, 1237, 1155, 1126, 802, 763, 746, 728.

***N*-(6-(3,3-Dimethylbutanamido)pyridin-2-yl)-3-((4-formyl-phenyl)ethynyl)benzamide (7).** To a solution of *N*-(6-acetamidopyridin-2-yl)-3,3-dimethylbutanamide (Hamilton receptor analogue: **5**) (300 mg, 0.76 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (4.00 mg, 0.0060 mmol), CuI (3.00 mg, 0.018 mmol) in THF/ HNEt_2 4-ethynylbenzaldehyde (118 mg, 0.91 mmol) were added at once. The reaction mixture was stirred for 20 h at room temperature. Then the precipitate was filtered, the solvent removed and the residue cleaned up by column chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{EtOAc}$ 5:1). Yield: 298 mg (98%). δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 10.01 (s, 1H), 8.25 (s, 1H), 8.05 (d, $^3J = 8.11$ Hz, 2H), 8.03 (d, $^3J = 7.94$ Hz, 1H), 7.88 (d, $^3J = 8.42$ Hz, 2H), 7.76 (m, 3H), 7.74 (d, $^3J = 8.30$ Hz, 1H), 7.71 (s, 2H, NH), 7.67 (t, $^3J = 6.70$ Hz, 1H), 2.23 (s, 2H), 1.09 (s, 9H). δ_{C} (100.5 MHz; CDCl_3 ; Me_4Si) 191.37 (1C), 170.24 (1C), 164.43 (1C), 149.58 (1C), 149.31 (1C), 140.96 (1C), 135.70 (1C), 135.16 (1C), 134.64 (1C), 132.19 (2C), 130.33 (1C), 129.62 (2C) 129.13 (1C), 128.90 (1C), 127.46 (1C), 123.46 (1C), 109.86 (1C), 109.61 (1C), 91.89 (1C), 89.72 (1C), 51.76 (1C), 31.34 (1C), 29.77 (3C). MS

(FAB, NBA): $m/z = 440 [M]^+$. IR (diamond, RT): $\nu_{\max}/\text{cm}^{-1}$ 1686, 1671, 1601, 1586, 1512, 1504, 1448, 1296, 1240, 1208, 799, 735, 726.

[*N,N'*-Bis[6-(3,3-dimethylbutyrylamino)pyridin-2-yl]-5-ethynyl-phenyl-4-formyl-isophthalamide]-*N*-methyl-pyrrolidine fullerene monoadduct (DRC₆₀) (8). A Hamilton receptor derivative **6** (100 mg, 0.15 mmol) was dissolved in dry THF (10 cm³) before toluene (200 cm³) was added. After addition of C₆₀ (160 mg, 0.220 mmol) the reaction mixture was stirred under inert conditions and in the dark for 20 min. Then sarcosine (16 mg, 0.179 mmol) was added and the reaction mixture was refluxed for 20 h. After cooling down to room temperature the solvent was partially removed under reduced pressure and the mixture poured onto a silica column (toluene → toluene/EtOAc 2:1). The obtained brown solid was further purified by dissolving in CS₂ and precipitating with n-pentane. Yield: 115 mg (54 %). δ_{H} (400 MHz; CS₂, CDCl₃, THF-*d*₈; Me₄Si) 9.45 (broad s, 2H, NH), 8.79 (broad s, 2H, NH), 8.37 (s, 1H), 8.18 (d, ³*J* = 6.61, 2H), 7.93 (d, ³*J* = 8.54, 4H), 7.65 (m, 4 H), 7.58 (d, ³*J* = 8.42 Hz, 2H), 5.00 (d, ²*J* = 9.23 Hz, 1H), 4.97 (s, 1H), 4.28 (d, ²*J* = 9.4 Hz, 1H) 2.81 (s, 4H), 2.79 (s, 3H), 1.04 (s, 18 H). δ_{C} (100.5 MHz; CS₂, CDCl₃, THF-*d*₈; Me₄Si) 170.77 (2C), 164.52 (2C), 151.08 (2C), 150.62 (1C), 147.88, 147.84, 147.09, 146.85, 146.78, 146.67, 146.50, 146.32, 146.12, 145.90, 145.83, 145.78, 145.30, 145.12, 144.91, 144.72, 143.57, 143.15, 142.85, 142.74, 142.68, 142.47, 142.13, 140.73, 140.51, 140.45, 138.88 (58C), 138.88 (2C), 137.60 (2C), 137.05 (2C), 134.10 (2C), 132.53 (2C), 130.13 (2C), 129.28 (1C), 126.84 (1C), 124.80 (1C), 123.99 (1C), 110.47 (2C), 110.24 (2C), 91.69 (1C), 89.02 (1C), 83.66 (1C), 70.47 (1C), 69.79 (1C), 50.98 (2C), 40.14 (1C), 31.59 (2C), 30.11 (6C). MS (FAB, NBA): $m/z = 1421 [M]^+$. λ_{\max} (CH₂Cl₂)/nm 432.41, 311.0, 301.7, 255.6, 230.0. FT-IR (diamond, RT): $\nu_{\max}/\text{cm}^{-1}$ 3006, 2990, 2360, 1698, 1683, 1558, 1541, 1521, 1507, 1473, 1456, 1276, 1261, 764, 750.

***N*-(6-(3,3-Dimethylbutanamido)pyridin-2-yl)3-(4-phenyl-ethynyl)benzamide-*N*-methyl-pyrrolidine-fullerene monoadduct (SRC₆₀) (9).** After dissolving the Hamilton receptor analogue **7** (89 mg, 0.20 mmol) in THF (3 cm³), toluene (350 cm³) and C₆₀ (190 mg, 0.26 mmol) were added. This mixture was stirred for 30 min under exclusion of air and light. Then sarcosine (23 mg, 0.26 mmol) was added and the solution was heated for 20 h under reflux. After cooling down to room temperature, a column chromatography on silica gel (toluene→toluene/EtOAc 2:1) was used to isolate the monoadduct. Dissolving the separated brown solid and precipitating with n-pentane leads to a brown powder. Yield: 100 mg (43%). δ_{H} (400 MHz; CS₂, CDCl₃; Me₄Si) 8.16 (s, 2H, NH), 8.03 (d, ³*J* = 8.02 Hz, 2H), 7.97 (d, ³*J* = 7.95 Hz, 1H), 7.96 (s, 1H), 7.94 (d, ³*J* = 8.08 Hz, 3H), 7.71 (t, ³*J* = 8.06 Hz, 1H), 7.66 (d, ³*J* = 7.79 Hz, 2H), 7.46 (t, ³*J* = 7.79 Hz, 2H), 5.00 (d, ²*J* = 9.38 Hz, 1H), 4.96 (s, 1H), 4.29 (d, ²*J* = 9.38 Hz, 1H), 2.83 (s, 3H), 2.22 (s, 2H), 1.10 (s, 9H). δ_{C} (100.5 MHz; CDCl₃; Me₄Si) 169.47 (1C), 163.84 (1C), 155.83 (1C), 153.59 (1C), 152.62 (1C), 149.34, 146.17, 147.11, 146.37, 146.18, 146.14, 146.11, 146.02, 145.96, 145.93, 145.77, 145.55, 145.42, 145.39, 145.31, 145.18, 145.15, 145.09, 145.05, 144.99, 144.53, 144.42, 144.22, 144.17, 142.99, 142.85, 142.54, 142.43, 142.06, 141.97, 141.91, 141.87, 141.81, 141.71, 141.67, 141.53, 141.39, 140.60, 140.08, 140.04, 139.79, 139.41, 137.64 (58 C), 136.75 (1C), 136.29 (1C), 135.77 (1C), 134.76 (2C), 131.91

(1C), 129.92 (2C) 129.19 (1C), 128.84 (1C), 126.76 (1C), 124.04 (1C), 122.79 (1C), 109.55 (1C), 109.37 (1C), 90.72 (1C), 88.95(1C), 83.06 (1C), 69.87 (1C), 68.80 (1C), 51.49 (1C), 39.85 (1C), 30.99 (1C), 29.63 (3C). MS (FAB, NBA): $m/z = 1187 [M]^+$. λ_{\max} (CH₂Cl₂)/nm 430.6, 308.9, 294.2, 255.2, 233.5. FT-IR (diamond, RT): $\nu_{\max}/\text{cm}^{-1}$ 2360, 2342, 1718, 1655, 1447, 1276, 1261, 764, 750.

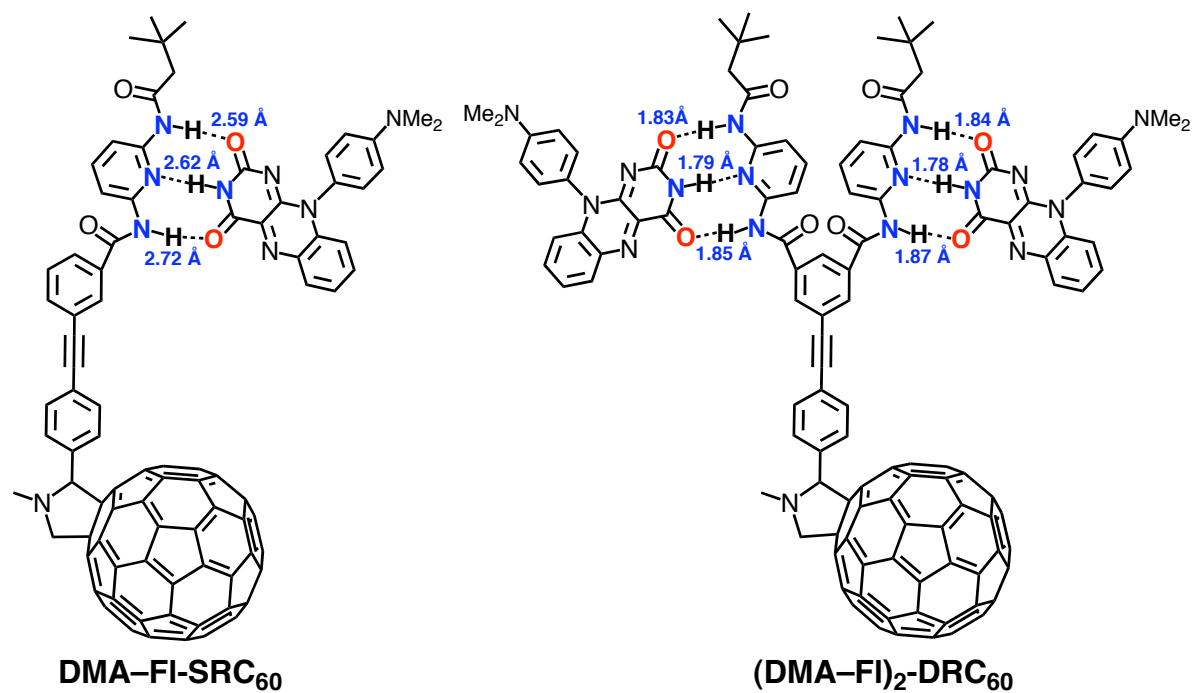


Fig. S2 Hydrogen-bond lengths in the optimized structure of DMA-FI-SRC₆₀ and (DMA-FI)₂-DRC₆₀ calculated by PM3.

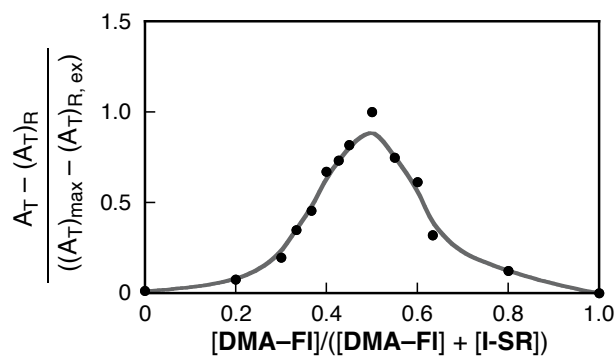


Fig. S3 Job's plot obtained by absorption band at 470 nm for the supramolecular complex formation between **DMA-FI** and **I-SR** in THF ($[\text{DMA-FI}] + [\text{I-SR}] = 9.0 \times 10^{-5} \text{ mol dm}^{-3}$).

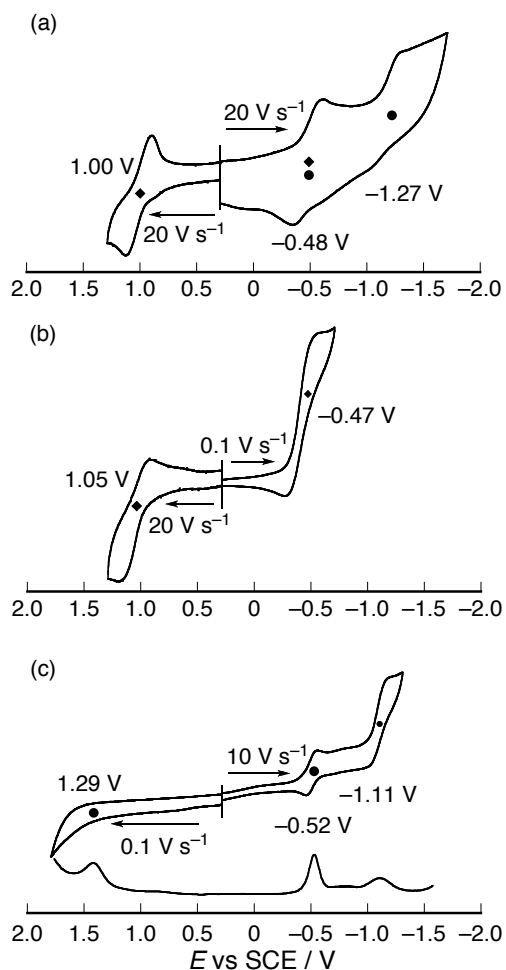


Fig. S4 (a) Cyclic voltammogram (CV) (sweep rate 20 V s⁻¹) with a platinum microelectrode (i.d. 100 μ m) of **DMA-FI** (2.0×10^{-3} mol dm⁻³) and **SRC₆₀** (2.0×10^{-3} mol dm⁻³), (b) CV (sweep rate 0.1 and 20 V s⁻¹) of **DMA-FI** (2.0×10^{-3} mol dm⁻³), and (c) CV (sweep rate 10 and 0.1 V s⁻¹) and differential pulse voltammogram (sweep rate 4 mV s⁻¹) of **SRC₆₀** (2.0×10^{-3} mol dm⁻³) in deaerated THF containing LiClO₄ (0.5 mol dm⁻³) at 298 K.

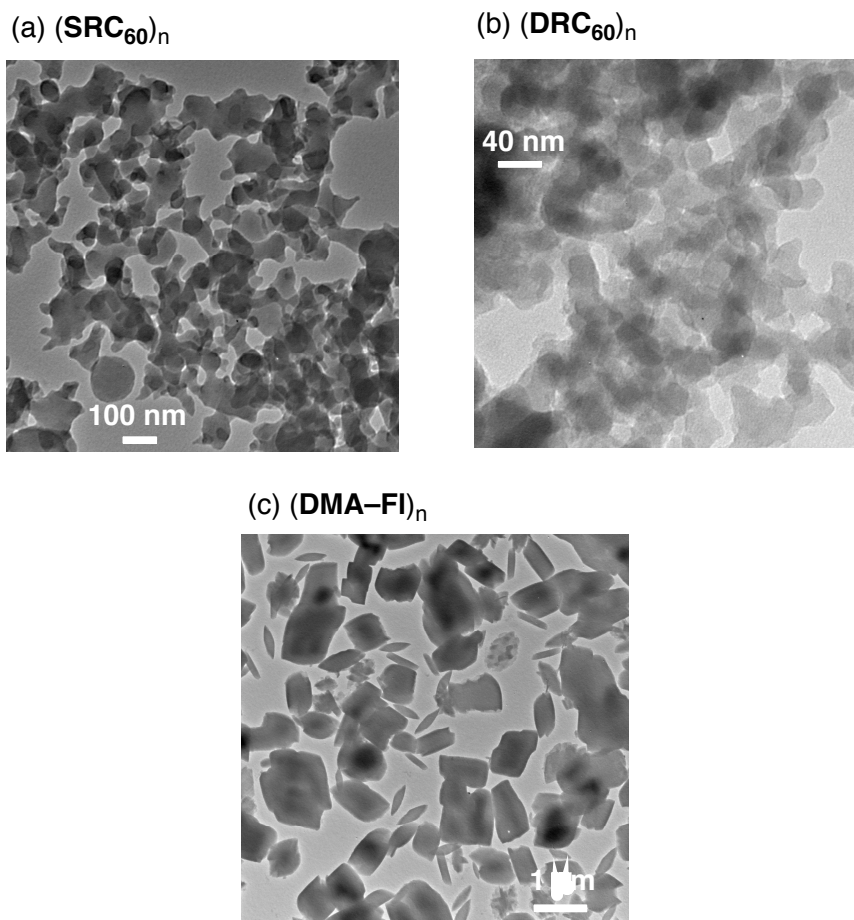


Fig. S5 TEM images of clusters prepared with (a) $[\text{SRC}_{60}] = 0.25 \text{ mmol dm}^{-3}$, (b) $[\text{DRC}_{60}] = 0.25 \text{ mmol dm}^{-3}$, and (c) $[\text{DMA-FI}] = 0.50 \text{ mmol dm}^{-3}$ in hexane/THF (3/1, v/v).

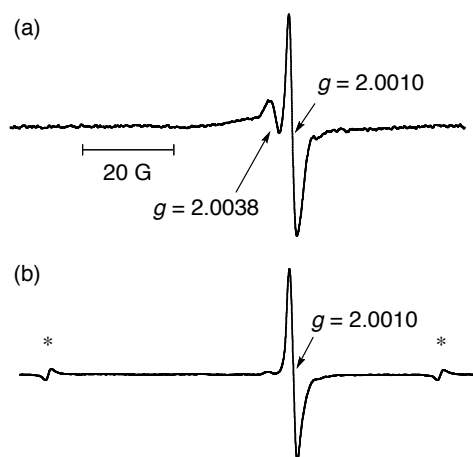


Fig. S6 ESR spectra of (a) photoirradiated $(\text{DMA-FI-SRC}_{60})_n$ ($[\text{DMA-FI}] = 0.25 \text{ mmol dm}^{-3}$; $[\text{SRC}_{60}] = 0.25 \text{ mmol dm}^{-3}$) in hexane/THF (3/1, v/v) with a high-pressure mercury lamp, (b) the radical anion of SRC_{60} clusters ($(\text{SRC}_{60})_n$) ($0.50 \text{ mmol dm}^{-3}$) generated in photoinduced electron transfer from dimeric 1-benzyl-1,4-dihydronicotinamide $[(\text{BNA})_2]$ ($0.50 \text{ mmol dm}^{-3}$) to SRC_{60} clusters in hexane/THF (3/1, v/v) under photoirradiation of a high-pressure mercury lamp, measured at 77 K. Asterisk denotes Mn^{2+} marker.

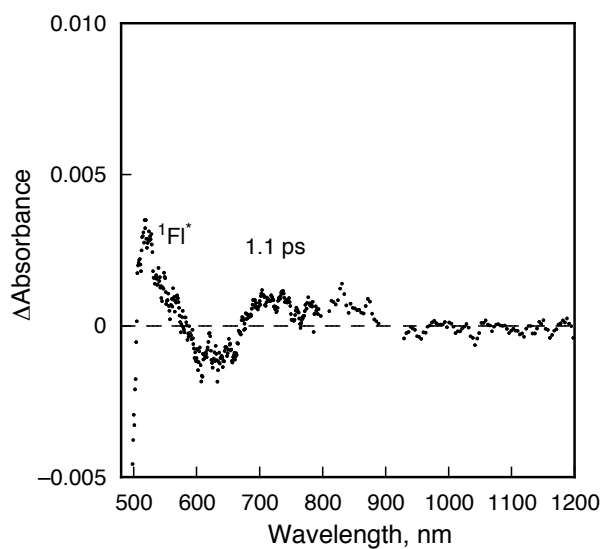


Fig. S7 Transient absorption spectra of $(10\text{-decylisalloxazine})_n$ clusters in KBr pellet taken at 1.1 ps after femtosecond laser excitation at 440 nm.

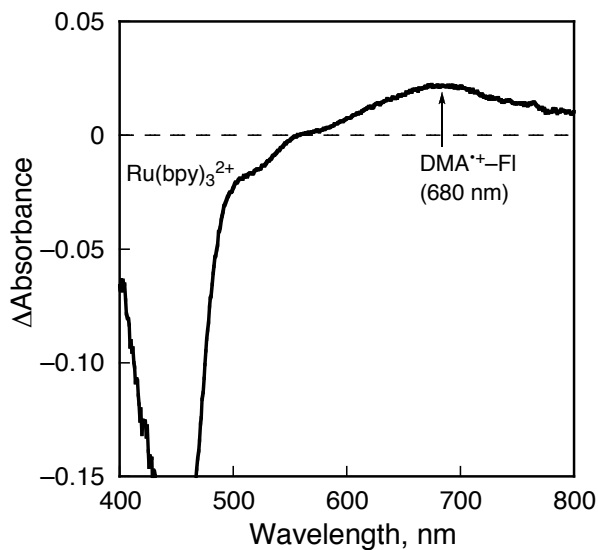


Fig. S8 Transient absorption spectrum observed in the electron-transfer oxidation of **DMA-FI** (5.0×10^{-5} mol dm⁻³) with [Ru(bpy)₃](PF₆)₃ (bpy = 2,2'-bipyridine) (5.0×10^{-5} mol dm⁻³) in deaerated MeCN at 2 ms at 298 K.

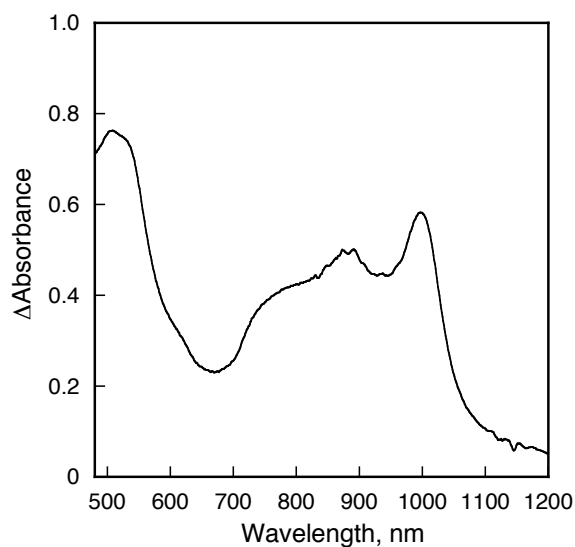


Fig. S9 Differential absorption spectrum of **DRC₆₀⁻** obtained in photo chemical reduction of **DRC₆₀** (1.3×10^{-4} mol dm⁻³) with (BNA)₂ (6.5×10^{-5} mol dm⁻³) in deaerated benzonitrile under irradiation of visible light ($\lambda > 400$ nm) at 298 K.

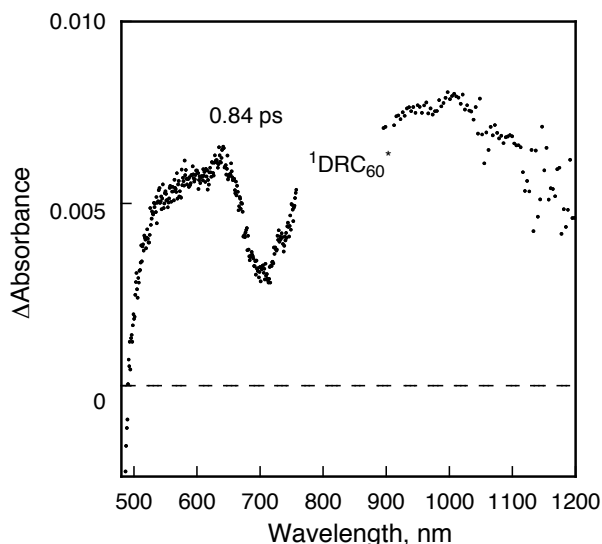


Fig. S10 Transient absorption spectra of $(\text{DRC}_{60})_n$ clusters in KBr pellet taken at 0.84 ps after femtosecond laser excitation at 440 nm.

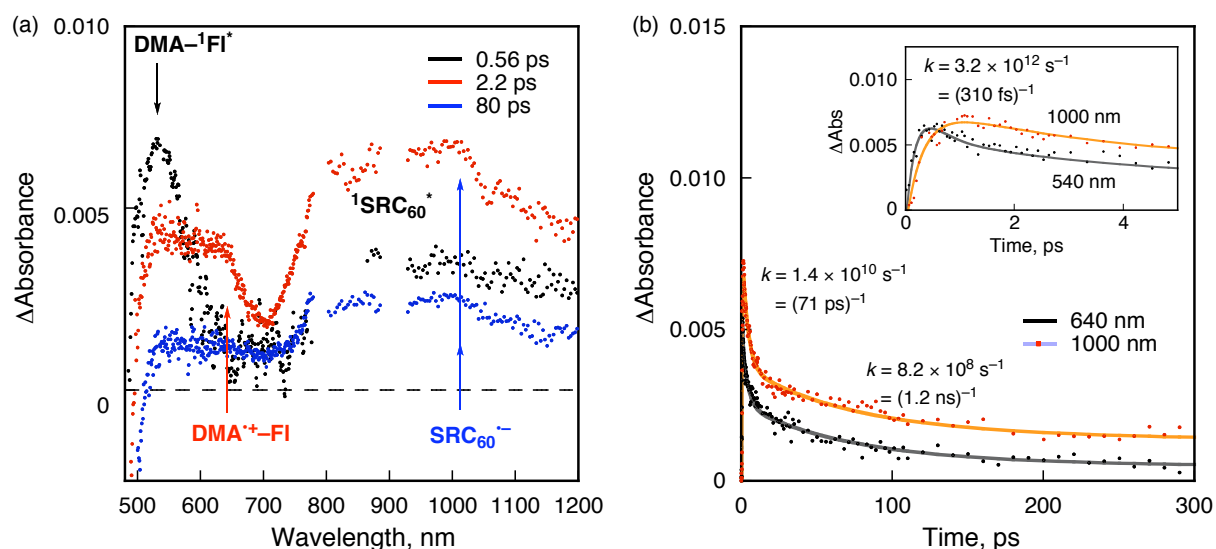


Fig. S11 (a) Transient absorption spectra of $(\text{DMA-FI-SRC}_{60})_n$ clusters in KBr pellet taken at 0.56 (black), 2.2 (red), and 80 ps (blue) after femtosecond laser excitation at 440 nm. (b) Time profiles of absorbance at 640 (black) and 1000 nm (red); inset: Time profiles at the shorter time range at 540 (black) and 1000 nm (red). The solid curves represent the best fit to the exponential rise or decay.