Tunneling versus Hopping in Mixed-Valence Oligo-*p*-Phenylenevinylene Polychlorinated Bis(triphenylmethyl) Radical-anions

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Supporting Information

Reference 1: Adams, D.M. et al.; Brus, L., Chidsey, C.E.D. ; Creager, S.; Creutz, C. ; Kagan, C.R. Prashant, Kamat, V.; Lieberman, M.; Lindsay, S.; Marcus, R.A. ; Metzger, R.M. ; Michel-Beyerle, M.E. ; Miller, J.R.; Newton, M. D. ; Rolison, D.R. ; Sankey, O. ; Schanze, K.S. ; Yardley, J. ; Zhu. X. *J. Phys. Chem. B* 2003, *107*, 6668.

Reference 43: Gaussian 03, Revision C.02, 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, V. Bakken, 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, Inc., Wallingford CT, 2004.

Preparation of compounds

Compound 18: Potassium *tert*-butoxide (0.08 g, 0.69 mmol) was added to a solution of **16** (0.41 g, 0.69 mmol) and **17** (0.3 g, 0.63 mmol) in dry THF (10 mL) under argon at 0°C. The mixture was stirred for 1h, then evaporated to dryness and taken up with CH_2Cl_2. The organic layer was washed with H_2O, dried over $MgSO_4$, filtered and evaporated to dryness. Column chromatography (SiO_2, hexane/CH_2Cl_2 3:2) gave **18** as an *E:Z* isomer mixture. The *E:Z* mixture obtained after the first chromatographic purification was directly isomerized as follows: a solution of the *E:Z* mixture and I_2 (5 mg, 0.02 mmol) in toluene (3 mL) was refluxed for 12 h and then cooled to room

temperature. The resulting toluene solution was washed with an aqueous 0.3 M $Na_2S_2O_3$ solution and water, dried over $MgSO_4$, filtered and evaporated to dryness. Column chromatography (SiO_2, hexane/CH_2Cl_2 3:2) gave **18** (0.45 g, 78%) as an orange powder. ^1H NMR (300 MHz, $CDCl_3$): 7.42 (s, 2 H), 7.18 (s, 2 H), 7.12 (s, 2 H), 5.75 (s, 2 H), 4.05-3.98 (m, 8 H), 3.72 (AB, $J = 11$ Hz, 8 H), 1.84-1.77 (m, 8 H), 1.49-1.27 (m, 46 H), 0.90-0.80 (m, 18 H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.03, 150.33, 128.46, 127.05, 123.85, 111.55, 110.60, 97.12, 77.89, 69.49, 69.39, 31.86, 31.83, 30.28, 29.46, 29.41, 29.38, 29.31, 26.20, 26.14, 23.23, 22.69, 22.65, 21.89, 14.08. Elemental analysis calc (%) for $C_{58}H_{96}O_8$: C 75.61, H 10.50; found: C 75.45, H 10.63.

Bisaldehyde 7: A mixture of **18** (0.42 g, 0.46 mmol) and CF_3CO_2H (10 mL) in CH_2Cl_2/H_2O 1:1 (20 mL) was stirred at room temperature for 4 h. The organic layer was then washed with water, dried over $MgSO_4$, filtered and evaporated to dryness. Column chromatography (SiO_2, hexane/CH_2Cl_2 3:2) gave **7** (0.25 g, 74%) as an orange powder. ^1H NMR (300 MHz, $CDCl_3$): 10.46 (s, 2 H), 7.59 (s, 2 H), 7.34 (s, 2 H), 7.19 (s, 2 H), 4.11 (t, $J = 6$ Hz, 4 H), 4.04 (t, $J = 6$ Hz, 4H), 1.88-1.83 (m, 8 H), 1.57-1.27 (m, 40 H), 0.87 (m, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$): 189.13, 156.10, 150.92, 134.04, 126.45, 124.66, 110.93, 110.17, 69.18, 69.07, 31.82, 31.79, 29.35, 29.33, 29.31, 29.26, 29.21, 26.13, 22.63, 14.06, 14.05. Elemental analysis calc (%) for $C_{48}H_{76}O_6$: C 76.96, H 10.23; found: C 76.69, H 10.41. FAB-MS: calcd. for $C_{48}H_{76}O_6$ 749.13; found 749.5 [MH$^+$].

Compound 19: Potassium *tert*-butoxide (0.04 g, 0.32 mmol) was added to a solution of **16** (0.36 g, 0.58 mmol) and **7** (0.22 g, 0.29 mmol) in dry THF (10 mL) under argon at 0°C. The mixture was stirred for 1h, then evaporated to dryness and taken up with CH_2Cl_2. The organic layer was washed with H_2O, dried over $MgSO_4$, filtered and evaporated to dryness. Column chromatography (SiO_2, hexane/CH_2Cl_2 3:2) gave **19** as an *E:Z* isomer mixture. The *E:Z* mixture obtained after the first chromatographic

purification was directly isomerized as follows: a solution of the *E:Z* mixture and I_2 (5 mg, 0.02 mmol) in toluene (3 mL) was refluxed for 12 h and then cooled to room temperature. The resulting toluene solution was washed with an aqueous 0.3 M $Na_2S_2O_3$ solution and water, dried over $MgSO_4$, filtered and evaporated to dryness. Column chromatography (SiO_2, hexane/CH_2Cl_2 3:2) gave **19** (0.2 g, 43%) as an orange powder which was used in the next step without further purifications. ^{1}H NMR (300 MHz, $CDCl_3$): 7.47 (d, *J* = 6 Hz, 6 H), 7.15 (t, *J* = 6 Hz, 8 H), 5.75 (s, 2 H), 4.08-3.98 (m, 16 H), 3.73 (AB, *J* = 11 Hz, 8 H), 1.84 (m, 16 H), 1.55-1.28 (m, 86 H), 0.86 (m, 30 H).

Bisaldehyde 9: A mixture of **19** (0.15 g, 0.09 mmol) and CF_3CO_2H (5 mL) in CH_2Cl_2/H_2O 1:1 (10 mL) was stirred at room temperature for 4 h. The organic layer was then washed with water, dried over $MgSO_4$, filtered and evaporated to dryness. Column chromatography (SiO_2, hexane/CH_2Cl_2 3:2) gave **9** (0.1 g, 75%) as an orange powder. ^{1}H NMR (300 MHz, $CDCl_3$): 10.46 (s, 2 H), 7.62 (AB, *J* = 16 Hz, 2 H), 7.52 (s, 2 H), 7.50 (AB, *J* = 16 Hz, 2H), 7.34 (s, 2 H), 7.22 (s, 2 H), 7.18 (s, 2 H), 7.16 (s, 2 H), 4.14-4.03 (m, 16 H), 1.91-1.84 (m, 16 H), 1.52-1.27 (m, 80 H), 0.88 (m, 24 H). ^{13}C NMR (75 MHz, $CDCl_3$): 189.16, 156.29, 151.44, 151.35, 151.08, 135.18, 128.31, 127.46, 127.00, 124.13, 123.27, 122.79, 110.93, 110.50, 110.36, 110.10, 69.50, 69.41, 69.15, 69.08, 31.89, 31.82, 29.71, 29.53, 29.48, 29.37, 29.34, 29.26, 26.30, 26.17, 22.67, 14.09. Elemental analysis calc (%) for $C_{96}H_{152}O_{10} \cdot H_2O$: C 77.68, H 10.46; found: C 77.58, H 10.55. MALDI-MS: calcd. for $C_{96}H_{152}O_{10}$ 1465.14; found 1465.04 [MH^+].

(*E,E*)-*p*-Divinyl(2,5-dioctiloxy)benzene-*β,β'*-ylene-bis(4-tetradecachlorotriphenylmethyl) diradical (1): Potassium *tert*-butoxide (0.0341g, 304.19 µmol) was added to a solution of the phosphonium bromide **15** (0.2199 g, 203.4 µmol) in dry tetrahydrofuran (15 mL). First the solution was cooled down in an ice bath and then the temperature was led rise to room temperature. The resulting

yellow and then orange-red ylide solution was stirred for 25 min. Then bisaldehyde **6** (0.0399 g, 102.31 µmol) in 8 ml of also dry THF was added at a constant drop flow, and the solution, which turned progressively purple, was stirred for 48 h. Then an aqueous solution of tetrabutylammonium hydroxide (0.47 mL, 705.00 µmol) was added. The resulting purple solution was stirred for 16 h. After this time, an excess of *p*-chloranil (0.1951 g, 790.89 µmol) was added and the stirring continued for a further 4 h. Elimination of the solvent gave a residue which was passed through silica gel, first in hexane and then with progressive amounts of mixing of hexane/dichloromethane to give the diradical **1** as a solid, which was stable in contact with the atmosphere at temperatures up to 150 °C (yield 61 %). IR (KBr): $\tilde{\nu}$ = 2918, 1613, 1508, 1336, 1258, 1202 cm^{-1}. Elemental analysis calc (%) for $C_{64}H_{40}O_2Cl_{28}$: C, 41.92; H, 2.20; found C, 42.12; H, 2.18. UV-Vis (CH$_2$Cl$_2$, $\lambda_{max,}$ nm (10^{-3} ε, M^{-1}cm^{-1})): 321 (15.7), 368 (sh), 388 (52.3), 418 (sh), 509 (11.8), 680 (3.8). MALDI-TOF/MS: 1832 (M$^+$). Cyclic voltammetry (CH$_2$Cl$_2$, V *vs* Ag/AgNO$_3$): E_{red} = -0.18; E_{ox} = 1.14. ESR (toluene/dichloromethane: 1/1): g = 2.0025; a $_{(2\,H)}$ = 0.88 Gauss; a ^{13}$_{C\alpha}$ = 14.8 Gauss; a (^{13}$_{Carom}$ = 6.5; 5.4 Gauss); $\Delta H_{\frac{1}{2}}$ = 0.88 Gauss at 220 K.

Bis[2,5-dioctiloxy-4-(*E*-vinylene-4-tetradecachlorotriphenylmethyl)-1-phenylene] (2): Potassium *tert*-butoxide (0.025 g, 223.01 µmol) was added to a solution of the phosphonium bromide **15** (0.1270 g, 117.47 µmol) in dry tetrahydrofuran (10 mL). First the solution was cooled down in an ice bath and then the temperature was led rise to room temperature. The resulting yellow and then orange-red ylide solution was stirred for 25 min. Then bisaldehyde **7** (0.044 g, 58.73 µmol) was added, and the solution, which turned progressively dark blue/green, was stirred for 72 h. Then an aqueous solution of tetrabutylammonium hydroxide (0.63 mL, 945.0 µmol) was added. The resulting dark green solution was stirred for 16 h. After this time, an excess of *p*-

chloranil (0.3466 g, 1409.64 µmol) was added and the stirring continued for a further 4 h. Elimination of the solvent gave a residue which was passed through silica gel for two times (first in hexane and then with progressive amounts of mixing of hexane/dichloromethane) to give the diradical **2** as a solid in a 15 % yield, and then the corresponding monoradical **11** in a 40 % yield which were stable in contact with the atmosphere at temperatures up to 150 °C. Diradical **2**: IR (KBr): $\bar{\nu}$ = 2924, 1602, 1503, 1336, 1202 cm^{-1}. Elemental analysis calc (%) for $C_{88}H_{78}O_4Cl_{28}$: C, 48.21; H, 3.59; found C, 48.13; H, 3.38. UV-Vis (CH_2Cl_2, λ_{max}, nm (10^{-3} ε, $M^{-1}cm^{-1}$)): 338 (21.1), 368 (sh), 389 (58.1), 434 (55.3), 547 (12.2), 757 (4.9). MALDI-TOF/MS ($C_{88}H_{78}O_4Cl_{28}$, M.W.: 2192.2 g/mol): 2192.9 (M$^+$). Cyclic voltammetry (CH_2Cl_2, V vs Ag/AgNO$_3$): E_{red} = -0.20; E_{ox} = 0.96. ESR (toluene/dichloromethane: 1/1): g = 2.0022; $a_{(2\ H)}$ = 0.88 Gauss; $a_{(2\ H)}$ = 0.34 Gauss; $a\ ^{13}C\alpha$ = 14.5 Gauss; $a\ (^{13}C_{arom}$ = 6.2; 5.1 Gauss), $\Delta H_{1/2}$ = 0.32 Gauss at 220 K. Monoradical **11**: IR (KBr): $\bar{\nu}$ = 2924, 1678, 1600, 1498, 1336, 1203 cm^{-1}. UV-Vis (CH_2Cl_2, λ_{max}, nm (10^{-3} ε, $M^{-1}cm^{-1}$)): 334 (20.9), 367 (sh), 390 (42.6), 427 (45.3), 542 (7.2), 745 (2.1). MALDI-TOF/MS ($C_{68}H_{77}O_5Cl_{14}$, M.W.: 1470.61 g/mol): 1470.0 (M$^+$). Cyclic voltammetry (CH_2Cl_2, V vs Ag/AgNO$_3$): E_{red} = -1.65, -0.19; E_{ox} = 1.05. ESR (toluene/dichloromethane: 1/1): g = 2.0020; $a_{(H)}$ = 1.80 Gauss; $a_{(H)}$ = 0.70 Gauss; $a\ ^{13}C\alpha$ = 29.1 Gauss; $a\ (^{13}C_{arom}$ = 12.7; 10.2 Gauss), $\Delta H_{1/2}$ = 0.56 Gauss at 220 K.

(E,E)-p-Divinyl(2,5-dioctiloxy)benzene-β,β'-ylene-bis[2,5-dioctiloxy-4-(E-vinylene-4-tetradecachlorotriphenylmethyl)-1-phenylene] (3): Potassium *tert*-butoxide (0.0133 g, 118.57 µmol) was added to a solution of the phosphonium bromide 15 (0.1085 g, 100.3 µmol) in dry tetrahydrofuran (15 mL). First the solution was cooled down in an ice bath and then the temperature was led rise to room temperature. The resulting yellow and then orange-red ylide solution was stirred for 25 min. Then bisaldehyde **8** (0.0505 g, 45.60 µmol) in 8 ml of also dry THF was added at a constant

drop flow, and the solution, which turned progressively dark green, was stirred for 114 h. Then an aqueous solution of tetrabutylammonium hydroxide (0.27 mL, 401.5 μmol) was added. The resulting purple solution was stirred for 16 h. After this time, an excess of *p*-chloranil (0.1086 g, 441.63 μmol) was added and the stirring continued for a further 4 h. Elimination of the solvent gave a residue which was passed through silica gel for two times (first in hexane and then with progressive amounts of mixing of hexane/dichloromethane) to give the diradical **3** as a solid in a 15 % yield, and then the corresponding monoradical **12** in a 53 % yield which were stable in contact with the atmosphere at temperatures up to 150 °C. Diradical **3**: IR (KBr): $\tilde{\nu}$ = 2921, 1594, 1504, 1337, 1259, 1202, 968, 816, 713, 668 cm^{-1}. UV-Vis (CH$_2$Cl$_2$, λ_{max}, nm (10^{-3} ε, M^{-1}cm^{-1})): 341 (27.4), 369 (sh), 390 (61.5), 454 (78.7), 558 (sh), 778 (5.7). MALDI-TOF/MS (C$_{112}$H$_{114}$O$_6$Cl$_{28}$, M.W.: 2548.8 g/mol): 2549.5 (M$^+$). Cyclic voltammetry (CH$_2$Cl$_2$, V *vs* Ag/AgNO$_3$): E_{red} = -0.22; E_{ox} = 0.86. ESR (toluene/dichloromethane: 1/1): g = 2.0022; a $_{(2\,H)}$ = 0.93 Gauss; a $_{(2\,H)}$ = 0.36 Gauss; a ^{13}$_{C\alpha}$ = 14.6 Gauss; a (^{13}$_{Carom}$ = 6.2; 5.1 Gauss), $\Delta H_{½}$ = 0.36 Gauss at 220 K. Monoradical **12**: IR (KBr): $\tilde{\nu}$ = 2921, 1675, 1594, 1504, 1338, 1202 cm^{-1}. Elemental analysis calc (%) for C$_{92}$H$_{115}$O$_6$Cl$_{14}$: C 60.40, H 6.35; found C 60.24, H 6.43. UV-Vis (CH$_2$Cl$_2$, λ_{max}, nm (10^{-3} ε, M^{-1}cm^{-1})): 339 (22.2), 368 (sh), 390 (44.2), 450 (72.1), 556 (sh), 776 (2.6). MALDI-TOF/MS (C$_{92}$H$_{115}$O$_6$Cl$_{14}$, M.W.: 1829.3 g/mol): 1829.7 (M$^+$). Cyclic voltammetry (CH$_2$Cl$_2$, V *vs* Ag/AgNO$_3$): E_{red} = -0.20; E_{ox} = 0.93. ESR (toluene/dichloromethane: 1/1): g = 2.0022; a $_{(H)}$ = 1.75 Gauss; a $_{(H)}$ = 0.70 Gauss; a ^{13}$_{C\alpha}$ = 28.9 Gauss; a (^{13}$_{Carom}$ = 12.7; 10.2 Gauss), $\Delta H_{½}$ = 0.62 Gauss at 220 K.

Bis-[(*E,E*)-*p*-Divinyl(2,5-dioctiloxy)benzene-β,β'-ylene]-bis[2,5-dioctiloxy-4-(*E*-vinylene-4-tetradecachlorotriphenylmethyl)-1-phenylene] **(4):** Potassium *tert*-butoxide (0.0281 g, 250.66 μmol) was added to a solution of the phosphonium bromide **15** (0.1329 g, 122.86 μmol) in dry tetrahydrofuran (10 mL). First the solution was

cooled down in an ice bath and then the temperature was led rise to room temperature. The resulting yellow and then orange-red ylide solution was stirred for 25 min. Then bisaldehyde **9** (0.060 g, 40.95 µmol) was added, and the solution, which turned progressively dark blue/green, was stirred for 110 h. Then an aqueous solution of tetrabutylammonium hydroxide (0.65 mL, 982.9 µmol) was added. The resulting dark green solution was stirred for 11 h. After this time, an excess of *p*-chloranil (0.3625 g, 1474.34 µmol) was added and the stirring continued for a further 4 h. Elimination of the solvent gave a residue which was passed through silica gel for two times, (first in hexane and then with progressive amounts of mixing of hexane/dichloromethane), to give the diradical **4** as a solid in a 11 % yield, and then the corresponding monoradical **13** in a 45 % yield which were stable in contact with the atmosphere at temperatures up to 150 °C. Diradical **4**: IR (KBr): $\tilde{\nu}$ = 2923, 1593, 1502, 1339, 1202 cm^{-1}; UV-Vis (CH$_2$Cl$_2$, $\lambda_{max,}$ nm (10^{-3} ε, M^{-1}cm^{-1})): 369 (sh), 389 (64.3), 462 (88.0), 579 (sh), 780 (6.2). MALDI-TOF/MS (C$_{136}$H$_{154}$O$_8$Cl$_{28}$, M.W.: 2909.39 g/mol): 2909.7 (M$^+$). Cyclic voltammetry (CH$_2$Cl$_2$, V *vs* Ag/AgNO$_3$): E_{red} = -0.22; E_{ox} = 0.82. ESR (toluene/dichloromethane: 1/1): g = 2.0024; $a_{(2\,H)}$ = 0.87 Gauss; $a_{(2\,H)}$ = 0.37 Gauss; a ^{13}Cα = 14.1 Gauss; a (^{13}C$_{arom}$ = 6.2; 5.3 Gauss), $\Delta H_{1/2}$ = 0.40 Gauss at 220 K. Monoradical **13**: IR (KBr): $\tilde{\nu}$ = 2923, 1676, 1593, 1502, 1338, 1203 cm^{-1}. UV-Vis (CH$_2$Cl$_2$, $\lambda_{max,}$ nm (10^{-3} ε, M^{-1}cm^{-1})): 333 (sh), 368 (sh), 389 (46.1), 462 (84.4), 574 (sh), 777 (2.3). MALDI-TOF/MS (C$_{116}$H$_{153}$O$_9$Cl$_{14}$, M.W.: 2187.7 g/mol): 2187.9 (M$^+$). Cyclic voltammetry (CH$_2$Cl$_2$, V *vs* Ag/AgNO$_3$): E_{red} = -0.20; E_{ox} = 0.83. ESR (toluene/dichloromethane: 1/1): g = 2.0022; $a_{(H)}$ = 1.80 Gauss; $a_{(H)}$ = 0.70 Gauss; a ^{13}Cα = 29.0 Gauss; a (^{13}C$_{arom}$ = 12.5; 10.1 Gauss), $\Delta H_{1/2}$ = 0.65 Gauss at 220 K.

Tris-[(*E,E*)-*p*-Divinyl(2,5-dioctiloxy)benzene-β,β'-ylene]-bis[2,5-dioctiloxy-4-(*E*-vinylene-4-tetradecachlorotriphenylmethyl)-1-phenylene] **(5):** Potassium *tert-*

butoxide (0.0212 g, 189.11 µmol) was added to a solution of the phosphonium bromide **15** (0.08898 g, 82.26 µmol) in dry tetrahydrofuran (8 mL). First the solution was cooled down in an ice bath and then the temperature was led rise to room temperature. The resulting yellow and then orange-red ylide solution was stirred for 25 min. Then bisaldehyde **10** (0.05992 g, 32.84 µmol) was added, and the solution, which turned progressively dark blue/green, was stirred for 100 h. Then an aqueous solution of tetrabutylammonium hydroxide (0.44 mL, 657.6 µmol) was added. The resulting dark green solution was stirred for 16 h. After this time, an excess of *p*-chloranil (0.2425 g, 986.40 µmol) was added and the stirring continued for a further 4 h. Elimination of the solvent gave a residue which was passed through silica gel for two times, (first in hexane and then with progressive amounts of mixing of hexane/dichloromethane) to give the diradical **5** as a solid in a 15 % yield, and then the corresponding monoradical **14** in a 50 % yield which were stable in contact with the atmosphere at temperatures up to 150 °C. Diradical **5**: IR (KBr): $\tilde{\nu}$ = 2925, 1597, 1500, 1340, 1202 cm^{-1}; UV-Vis (CH$_2$Cl$_2$, $\lambda_{max,}$ nm (10-3 (, M-1cm-1)): 334 (34.3), 369 (sh), 389 (69.1), 475 (121.9), 585 (sh), 782 (5.9). MALDI-TOF/MS (C160H192O10Cl28, M.W.: 3267.95 g/mol): 3268.8 (M+). Cyclic voltammetry (CH2Cl2, V vs Ag/AgNO3): Ered = -0.18; Eox = 0.80. ESR (toluene/dichloromethane: 1/1): g = 2.0023; a (2 H) = 0.90 Gauss; a (2 H) = 0.38 Gauss; a 13C(= 13.6 Gauss; a (13Carom = 6.2; 5.4 Gauss), (H½ = 0.40 Gauss at 230 K. Monoradical 14: IR (KBr): $\tilde{\nu}$ = 2923, 1678, 1593, 1501, 1339, 1205 cm-1. UV-Vis (CH2Cl2, (max, nm (10-3 (, M-1cm-1)): 333 (28.1), 368 (sh), 390 (47.8), 473 (116.2), 582 (sh), 780 (2.9). MALDI-TOF/MS (C$_{140}$H$_{191}$O$_{11}$Cl$_{14}$, M.W.: 2546.4 g/mol): 2546.0 (M+). Cyclic voltammetry (CH2Cl2, V vs Ag/AgNO3): Ered = -0.18; Eox = 0.78. ESR (toluene/dichloromethane: 1/1): g = 2.0023; a (H) = 1.80 Gauss; a (H) = 0.70

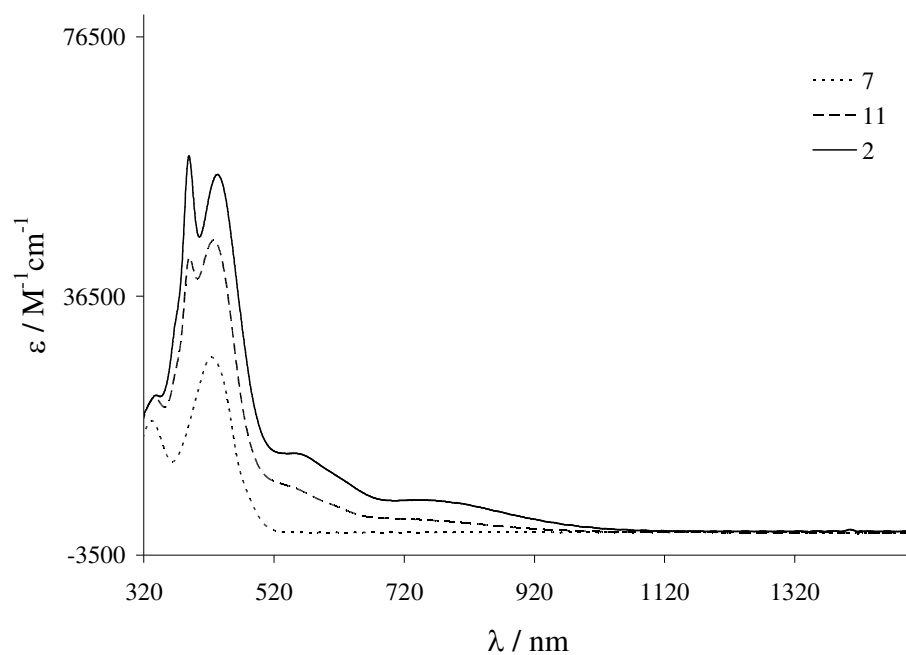Gauss; a 13C(= 29.3 Gauss; a (13Carom = 12.5; 10.2 Gauss), (H½ = 0.69 Gauss at 240

K.

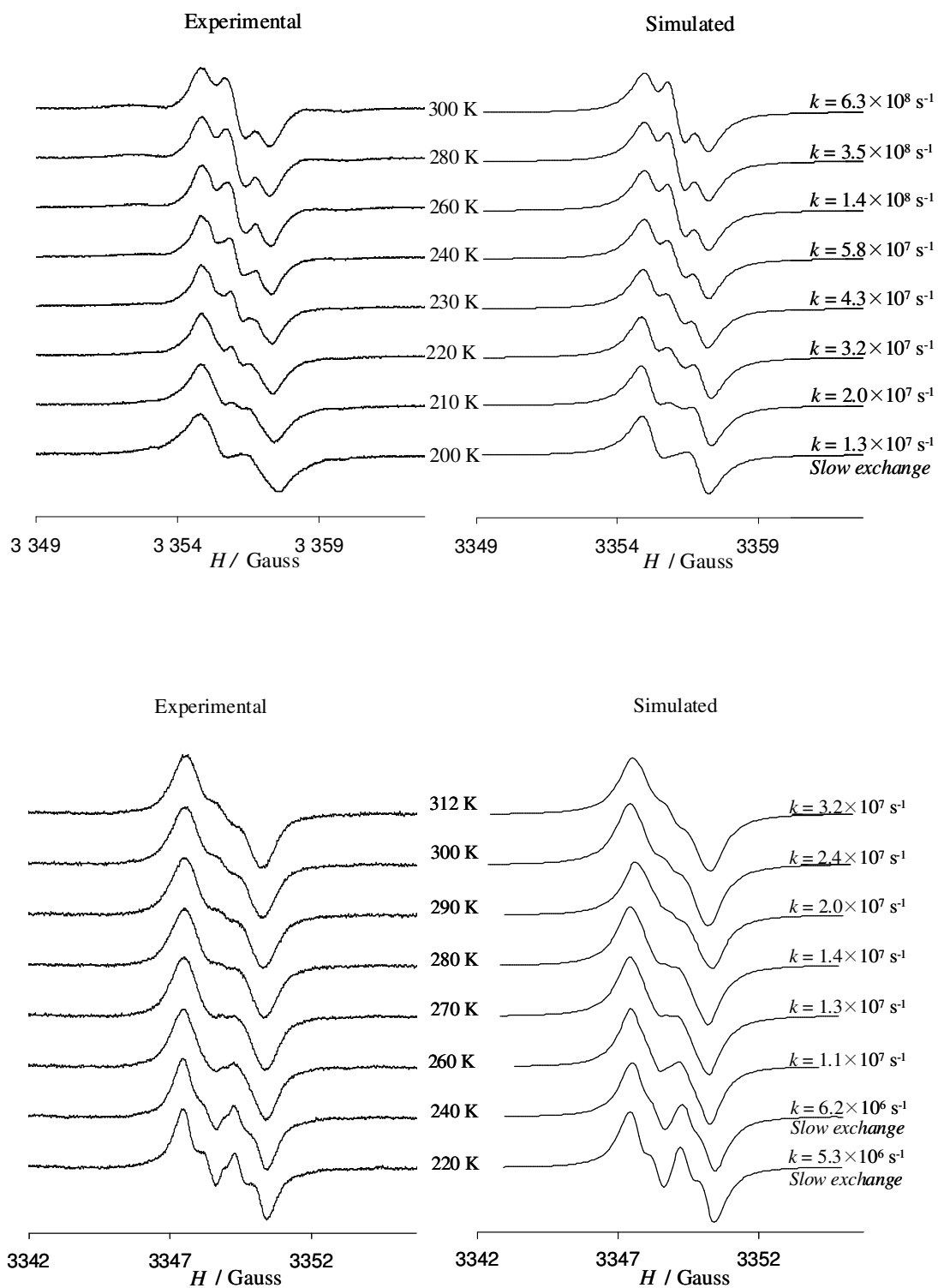**Figure S1.** Comparison of UV-Vis spectra of compounds **2**, **7** and **11** in CH$_2$Cl$_2$.

Experimental

Simulated

300 K — $k = 6.3 \times 10^8$ s^{-1}

280 K — $k = 3.5 \times 10^8$ s^{-1}

260 K — $k = 1.4 \times 10^8$ s^{-1}

240 K — $k = 5.8 \times 10^7$ s^{-1}

230 K — $k = 4.3 \times 10^7$ s^{-1}

220 K — $k = 3.2 \times 10^7$ s^{-1}

210 K — $k = 2.0 \times 10^7$ s^{-1}

200 K — $k = 1.3 \times 10^7$ s^{-1}
Slow exchange

3 349   3 354   3 359
H / Gauss

3349   3354   3359
H / Gauss

Experimental

Simulated

312 K — $k = 3.2 \times 10^7$ s^{-1}

300 K — $k = 2.4 \times 10^7$ s^{-1}

290 K — $k = 2.0 \times 10^7$ s^{-1}

280 K — $k = 1.4 \times 10^7$ s^{-1}

270 K — $k = 1.3 \times 10^7$ s^{-1}

260 K — $k = 1.1 \times 10^7$ s^{-1}

240 K — $k = 6.2 \times 10^6$ s^{-1}
Slow exchange

220 K — $k = 5.3 \times 10^6$ s^{-1}
Slow exchange

3342   3347   3352
H / Gauss

3342   3347   3352
H / Gauss

Figure S2. Experimental (left) and simulated (right) EPR spectra of **1$^{-•}$** (top) and **3$^{-•}$** (bottom) at different temperatures in CH$_2$Cl$_2$ with 0.1 M of [(Ph)$_4$P]Br.
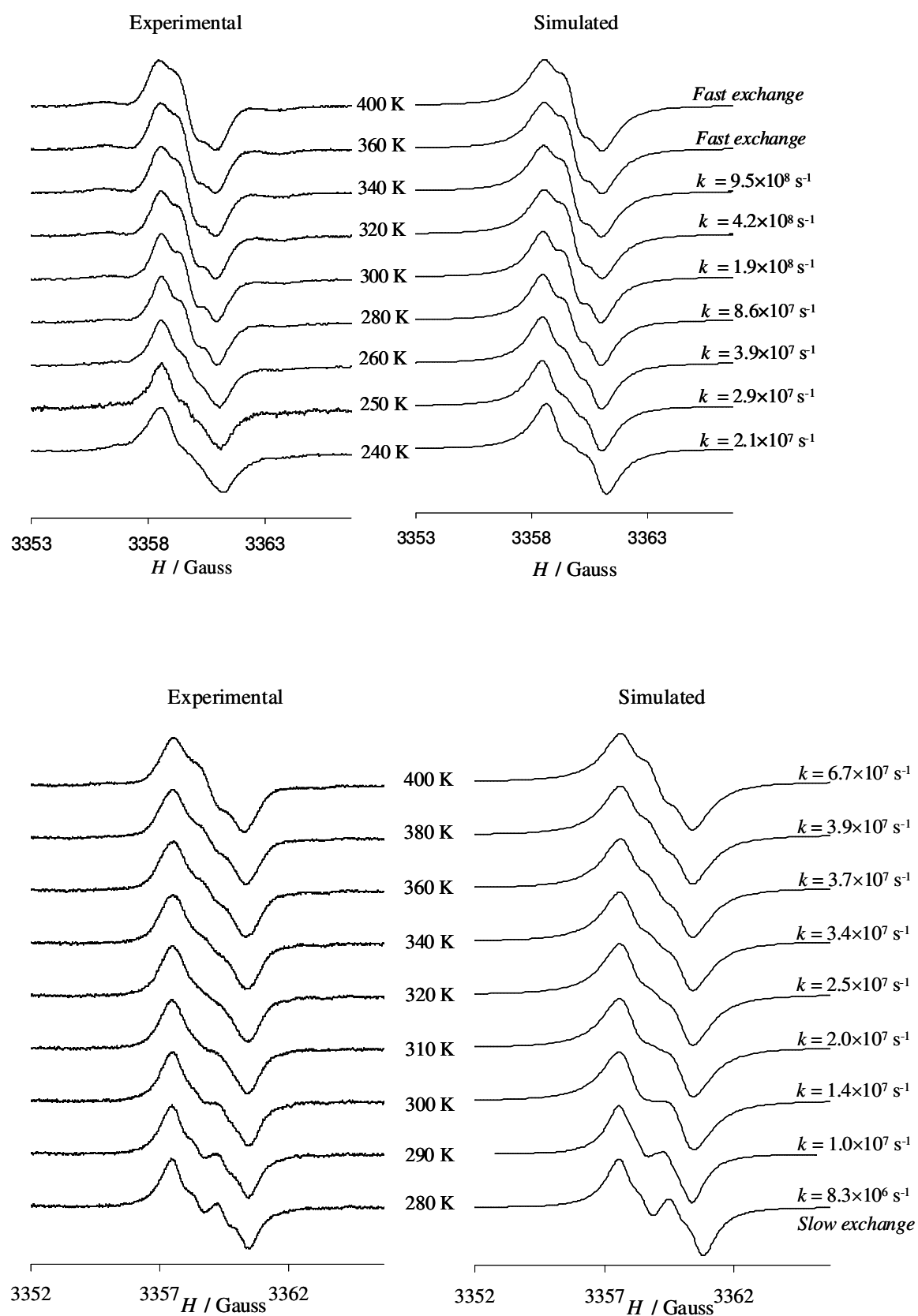
Figure S3. Experimental (left) and simulated (right) EPR spectra of **1**$^{-\bullet}$ (top) and **3**$^{-\bullet}$ (bottom) at different temperatures in 1,2-dichlorobenzene with saturated [(Ph)$_4$P]Br.
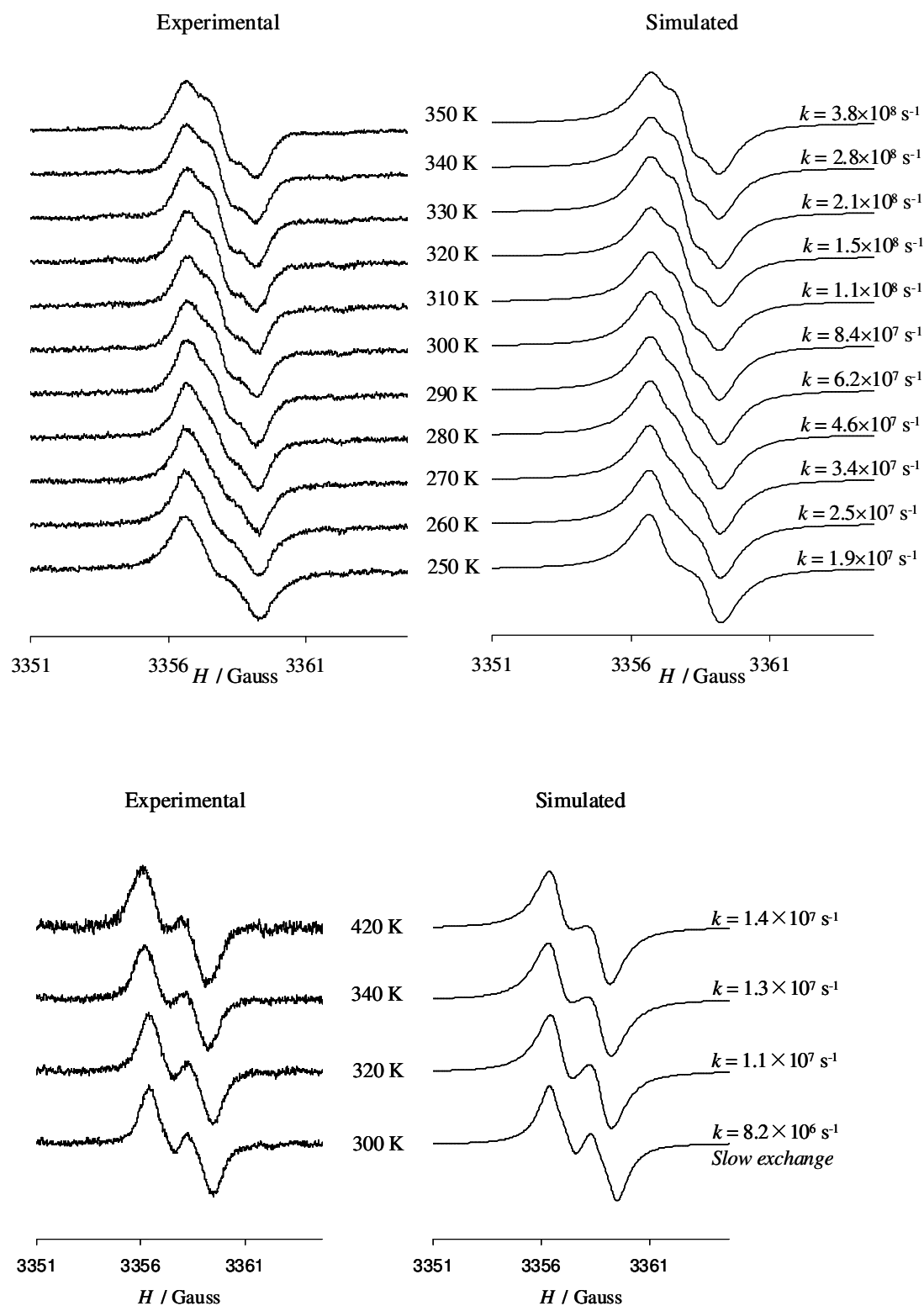
Figure S4. Experimental (left) and simulated (right) EPR spectra of **2^{-•}** (top) and **5^{-•}** (bottom) at different temperatures in 1,2-dichlorobenzene with saturated [(Ph)$_4$P]Br.
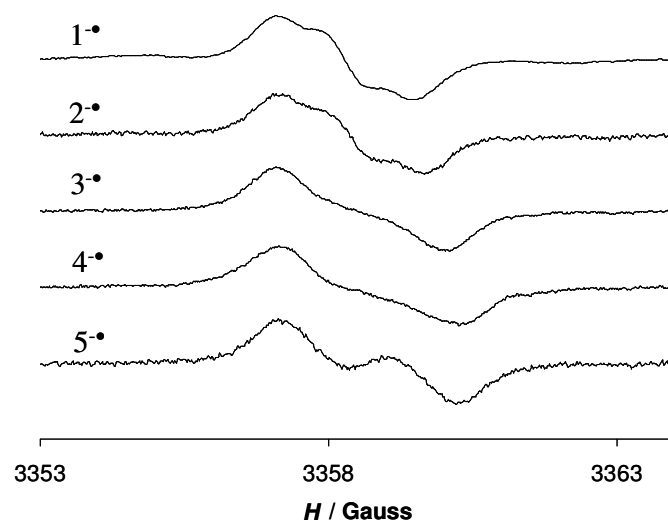
Figure S5. EPR spectra of **1⁻•** to **5⁻•** at 320 K in 1,2-dichlorobenzene, with saturated (PPh₄)Br.

Experimental

Simulated

380 K $\quad k = 9.6\times10^7\,\text{s}^{-1}$

360 K $\quad k = 7.1\times10^7\,\text{s}^{-1}$

340 K $\quad k = 5.3\times10^7\,\text{s}^{-1}$

320 K $\quad k = 3.5\times10^7\,\text{s}^{-1}$

300 K $\quad k = 2.1\times10^7\,\text{s}^{-1}$

280 K $\quad k = 1.2\times10^7\,\text{s}^{-1}$

260 K $\quad k = 3.9\times10^6\,\text{s}^{-1}$
Slow exchange

240 K $\quad k = 2.9\times10^6\,\text{s}^{-1}$
Slow exchange

3347 $\quad$ 3352 $\quad$ 3357
H / Gauss

3347 $\quad$ 3352 $\quad$ 3357
H / Gauss
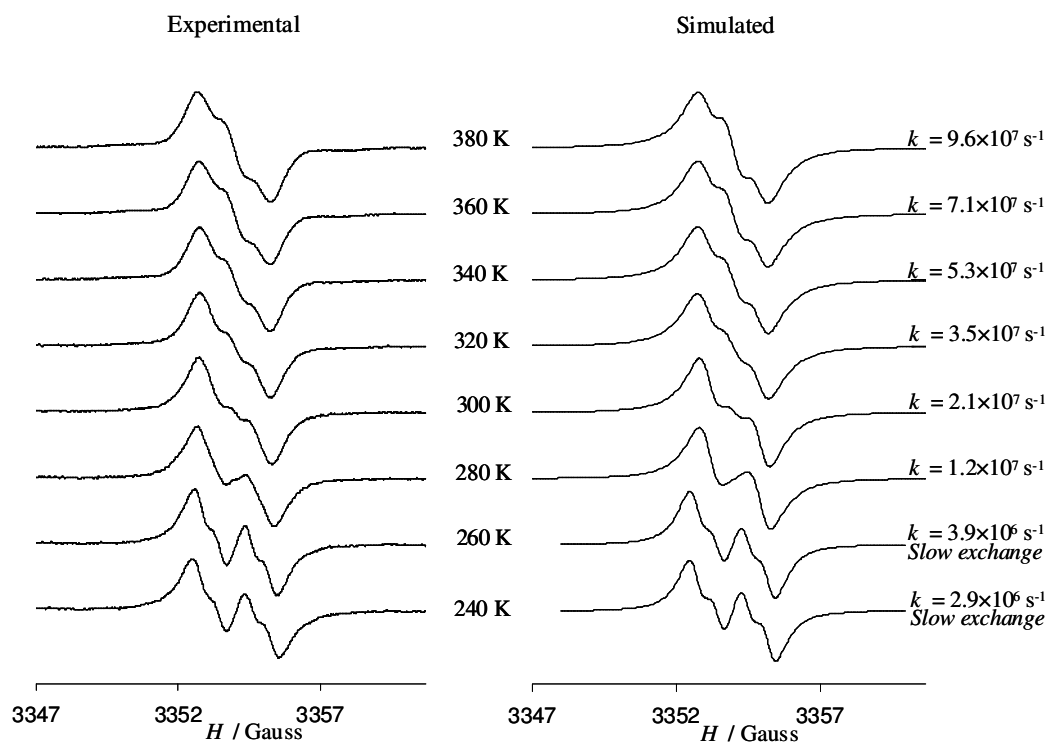
Figure S6. Experimental (left) and simulated (right) EPR spectra of **1**$^{-\bullet}$ at different temperatures in anisole with saturated [(Ph)$_4$P]Br.

Experimental

Simulated

340 K $\quad$ *Fast exchange*

320 K $\quad$ *Fast exchange*

300 K $\quad$ *Fast exchange*

280 K $\quad k = 4.3\times10^8\,\text{s}^{-1}$

260 K $\quad k = 1.6\times10^8\,\text{s}^{-1}$

240 K $\quad k = 7.2\times10^7\,\text{s}^{-1}$

230 K $\quad k = 5.3\times10^7\,\text{s}^{-1}$

220 K $\quad k = 3.9\times10^7\,\text{s}^{-1}$

210 K $\quad k = 2.6\times10^7\,\text{s}^{-1}$

200 K $\quad k = 1.6\times10^7\,\text{s}^{-1}$

3352 $\quad$ 3357 $\quad$ 3362
H / Gauss

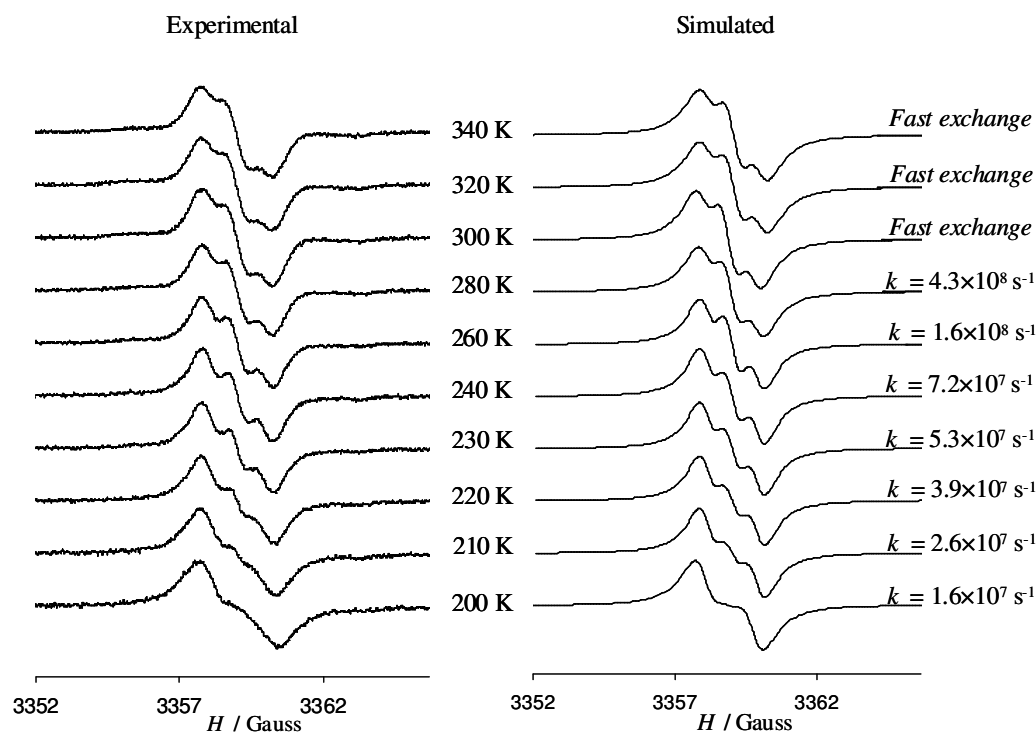3352 $\quad$ 3357 $\quad$ 3362
H / Gauss

Figure S7. Experimental (left) and simulated (right) EPR spectra of **1**$^{-\bullet}$ at different temperatures in ethyl acetate with saturated [(Ph)$_4$P]Br.
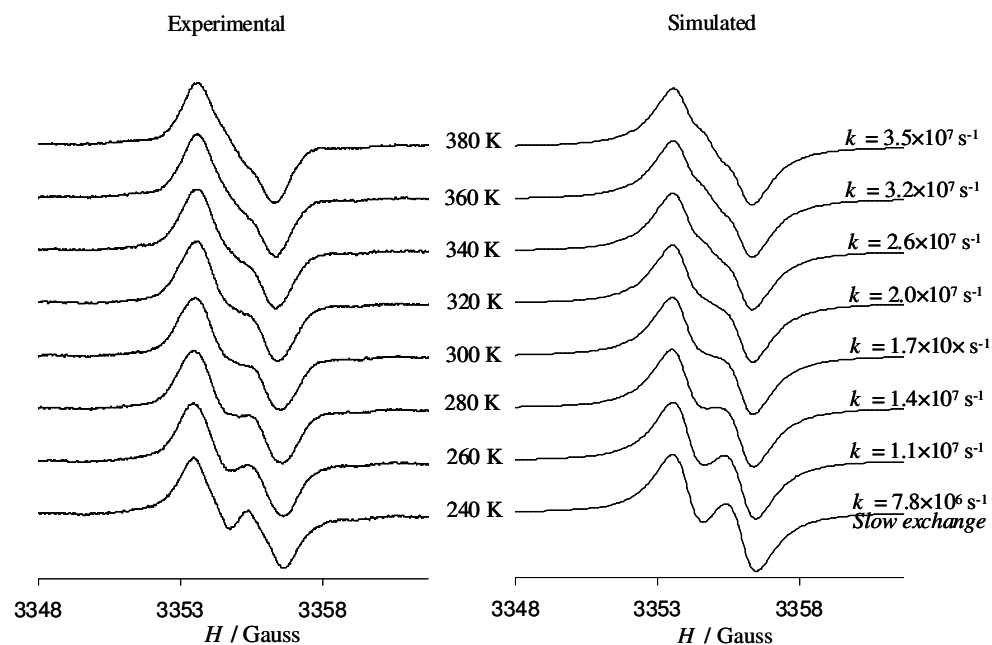
Figure S8. Experimental (left) and simulated (right) EPR spectra of **1**$^{-\bullet}$ at different temperatures in toluene with saturated [(Ph)$_4$P]Br.
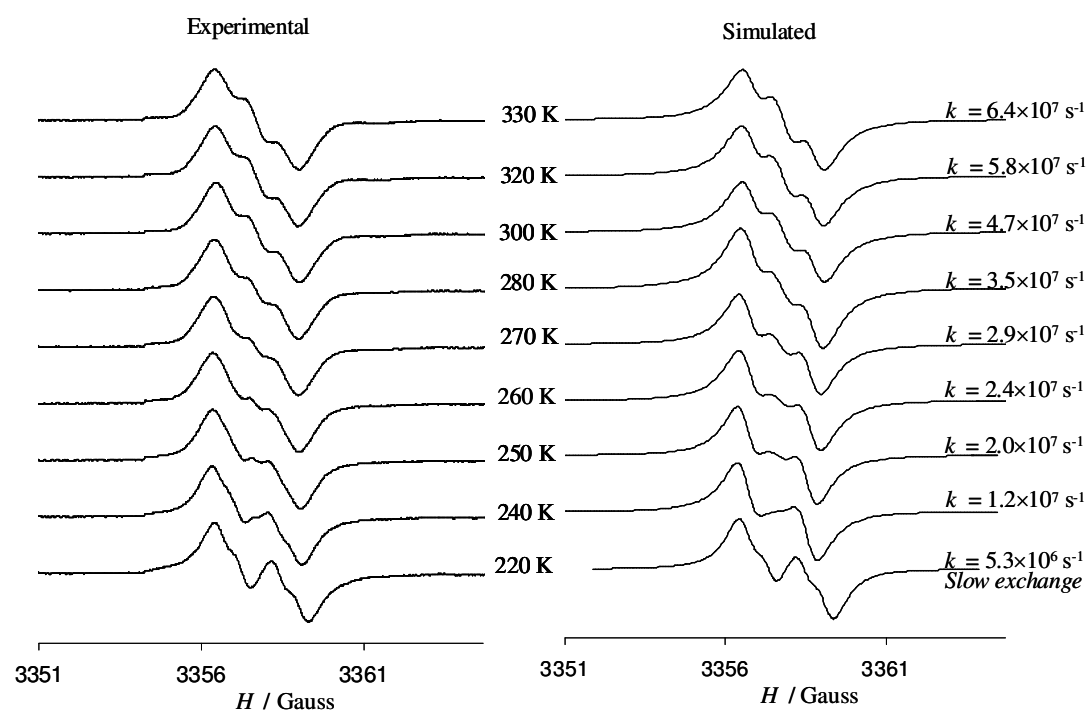

Figure S9. Experimental (left) and simulated (right) EPR spectra of **1**$^{-\bullet}$ at different temperatures in chloroform with 0.1 M [(Ph)$_4$P]Br.
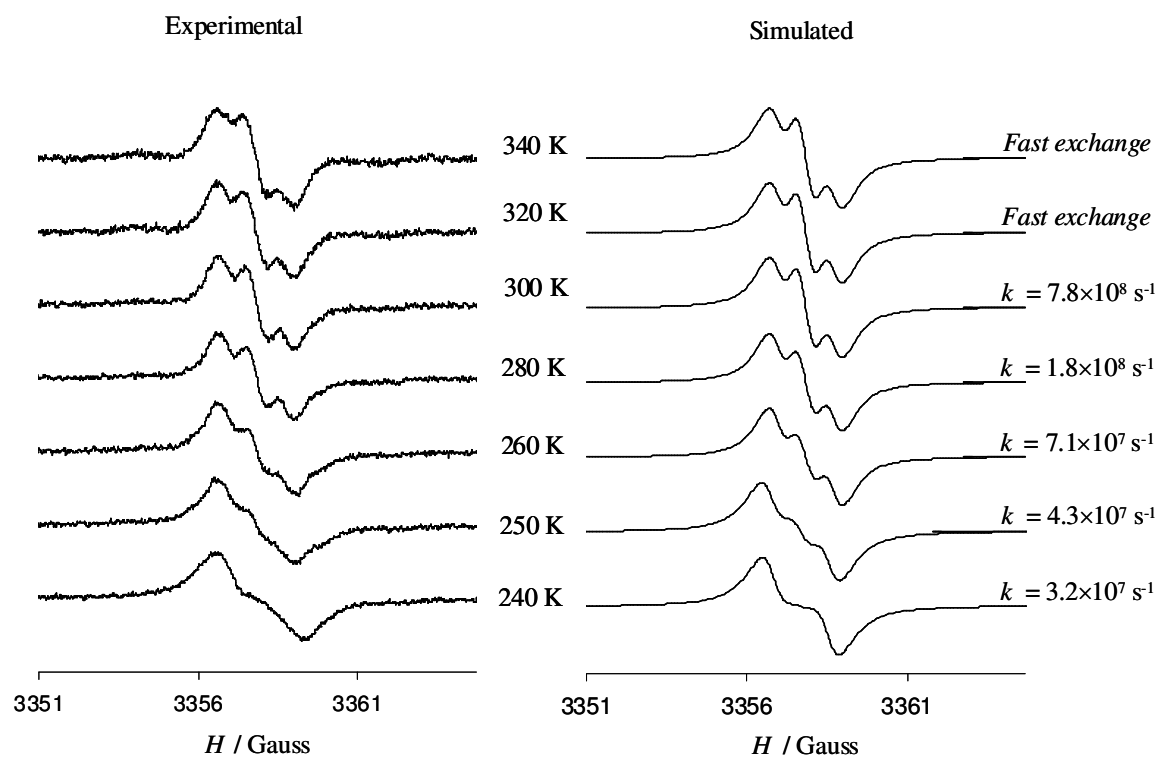
Figure S10. Experimental (left) and simulated (right) EPR spectra of **1**$^{-\bullet}$ at different temperatures in benzonitrile with 0.1 M [(Ph)$_4$P]Br.

Theoretical studies of radical anions 1[-•]-4[-•]. Most theoretical studies carried out up to now on IET were done employing one of the gradient-corrected density functional (DFT) methods.[1] Given the size of the systems of interest here this was also out first choice. However, the geometry optimization of the radical anion **1[-•]**, using the B3LYP functional and the 3-21G basis set and in which the two octyloxy groups were replaced by methoxy groups for reducing the computational costs, gave as results a completely symmetric molecule where the electron density was equally shared in the two halves of the radical anion. This result, which agrees with the well know tendency of B3LYP wavefunctions to over-delocalize the orbitals in the π subsystem, is not in agreement with the experimental evidence showing that **1[-•]** belongs to the Class II mixed-valence compound (*vide supra*) with an asymmetrical electronic distribution. This failure of the B3LYP functional to predict the right class for charge-transfer compounds is in good agreement with the predictions found by Renz et al.[1a] We did not try to include solvent effects in the continuous model, as done in this reference. Indeed, we have found that solvent effects in our experiments were not important, at least in the low polarity solvents employed here.

After a series of systematic tests using other methods, we found that ROHF and CASSCF calculations using (3,3), (5,5) and (7,7) complete active spaces and the 3-21G basis sets gave data in agreement with the experimental observations. The (3,3) active space, the smallest one, was built by selecting the delocalized SOMO found in the B3LYP calculation, its closest doubly occupied orbital and the nearest empty orbital of π symmetry. The occupation of these three orbitals in the B3LYP calculation was 2.0, 1.0, and 0.0, which became 1.91, 1.0 and 0.09 in the CASSCF(3,3) calculations. The orbitals for the CASSCF(5,5) and CASSCF(7,7) calculations were done by adding

occupied and empty orbital, appropriately (the orbital occupation of the (7,7) space is 1.99, 1.93, 1.90, 1.99, 0.10, 0.07 and 0.01).

Even when using the symmetric optimum B3LYP/3-21G geometry, these CASSCF(3,3) calculations predicted a non symmetrical distribution of the electron density on the two halves of the radical anion model of $1^{-\bullet}$, in good agreement with the experimental data. As shown in Figure S11, the same electron localized electronic distribution is found in CASSCF(7,7), clearly appreciated by looking at the SOMO orbital (active orbital 4, with occupation 1.00). Given such a charge localization, it was not a surprise that a ROHF/3-21G and a CASSCF(3,3)/3-21G geometry optimization of the optimum B3LYP/3-21G geometry ended in an optimum asymmetric structure; the largest change for the distances is found for the Csp^2 atom of the PTM units, whose Csp^2-C(central-six-membered ring) is in one case 0.04 Å larger than in the other. These CASSCF(3,3) predictions were confirmed by the more accurate CASSCF(7,7) computations. ROHF/3-21G calculations gave also the same results.
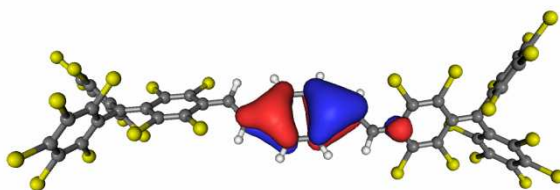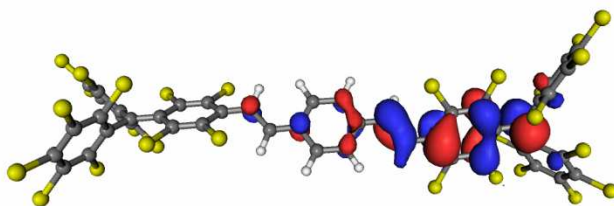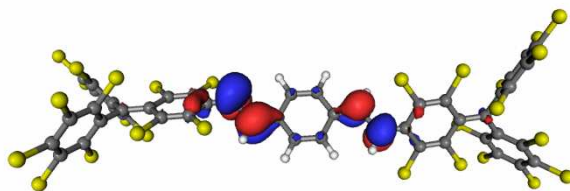

active=1 (orb=384); oc=1.99
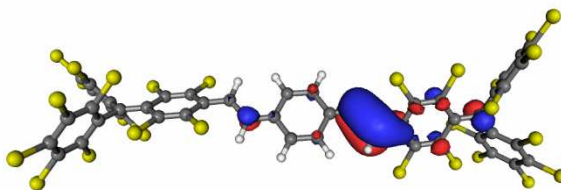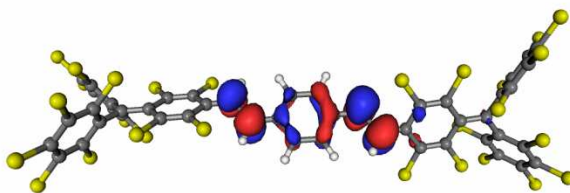

active=2 (orb=385); oc=1.93
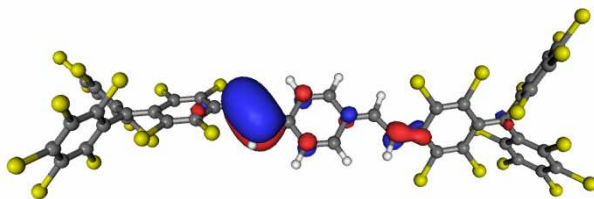
active=3 (orb=386); oc=1.90
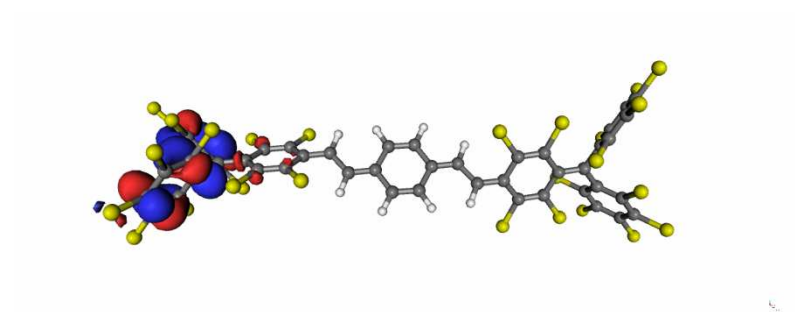

active=4 (orb=387); oc=1.00

active=5 (orb=388); oc=0.10

active=6 (orb=389); oc=0.08

active=7 (orb=390); oc=0.01

Figure S11. Shape and occupation of the seven active orbitals of the CASSCF(7,7) calculation. For each orbital, its number in the set of orbitals is also given in parenthesis
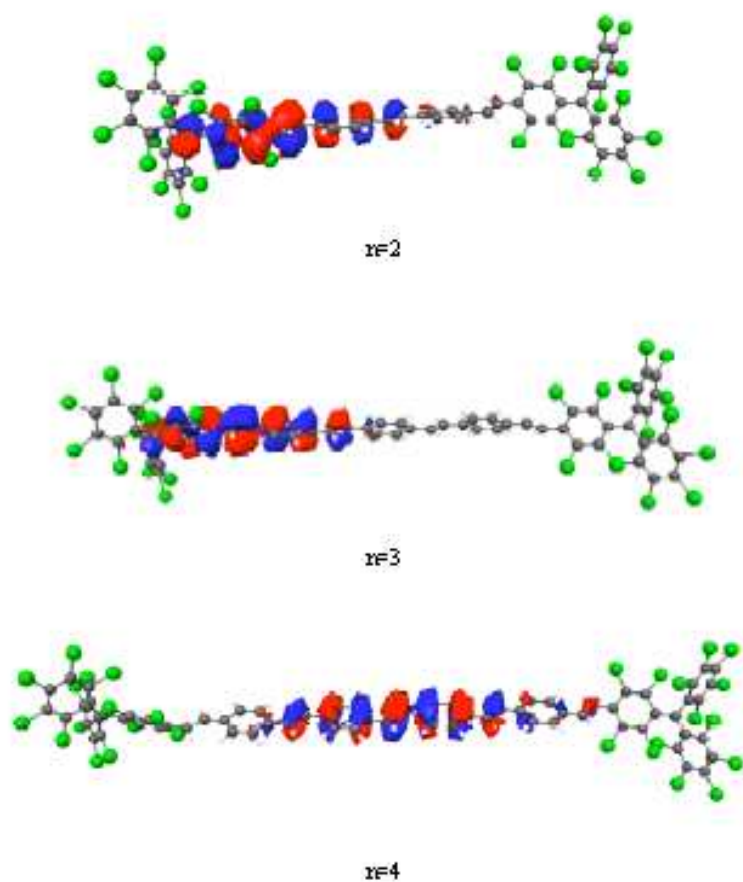
Figure S12. Shapes of the SOMO orbital for radical anions **2^{-•}** , **3^{-•}** and **4^{-•}** obtained by ROHF calculations for the (45, 45) point as the number of central connecting rings is increased.

Table S1. Kinetic data,[a] obtained from VT-ESR experiments at the high-T region for IET processes of radical anion $1^{-\bullet}$ in different solvents, and solvent parameters.

Solvent	A	E_a	π^*	α	δ
Ethyl acetate	3.22×10^{13}	6.24	0.55	0	0
CH_2Cl_2	1.12×10^{13}	5.81	0.82	0.13	0.5
Benzonitrile	9.70×10^{14}	8.57	0.90	0	1.0
1,2-$C_6H_4Cl_2$	6.38×10^{13}	7.55	0.80	0	1.0
$CHCl_3$	2.59×10^{9}	2.41	0.58	0.2	0.5
Toluene	4.81×10^{8}	1.98	0.54	0	1.0
Anisole	3.54×10^{10}	4.43	0.73	0	0

[a] A, in s^{-1}; E_a, in $kcal \cdot mol^{-1}$

Study of the influence of solvents on the IET of radical anion 1$^{\cdot-}$

This study has been done with a Linear Solvation Energy Relationship (LSER)[2,3,4] analysis of the thermal energy barrier, E_a, of the mixed-valence species **1$^{\cdot-}$** in different solvents. The LSER theory relates the energy changes of a given molecular process that takes place in solution with several specific and non-specific properties of the solvents in which the process is carried on. LSER assumes linear relationships for each of the contributing terms to the observed solvent effects, and presumes that each term is independent and additive. The LSER equation used adopts the form of Equation 1.

$$E_a = E_a{}^0 + s(\pi^* + d\delta) + a\alpha + b\beta + e\xi \tag{1}$$

As mentioned before, the experimental value used to characterize the IET process in this analysis is the activation energy barrier, E_a. In this expression, the independent term $E_a{}^0$ represents the thermally activated energy barrier in an "ideal" non-interactive solvent, in which all the solvatochromic parameters are null, and therefore is the expected value for the barrier in vaccum. On the other hand, π^*, δ, α, β and ξ are descriptive empirical solvatochromic parameters describing the solvent: π^* corresponds to a measure of the solvent polarity-polarizability,[5] δ is a discontinuous "polarizability correction" term for certain solvent types,[6] α is a measure of the solvent hydrogen-bond donor acidity and describes the ability of a solvent to accept an electron pair in a solvent-solute interaction,[7] β parameter refers to the hydrogen-bond acceptor (HBA) basicity of the solvent and describes the ability of a solvent to donate an electron pair in a solvent-solute interaction,[8] and ξ is a coordinate covalency parameter useful in correlating certain types of basicity properties.[9,10] Coefficients s, d, a, b and e are characteristic of

the intramolecular electron transfer process of the mixed-valence species under study being independent of the solvent. These coefficients are indicative of the sensitivity of IET process towards each solvent property ($\pi*$, δ, α, β and ξ) variation. Coefficients with a negative sign, point out that an increase of the associated solvent-solute interaction strength causes an energy barrier decrease. On the contrary, coefficients with positive sign indicate that an increase of the associated solvent-solute interaction strength that provokes an energy increase of the thermal electron transfer. Coefficients s, d, a, b and e and the independent term $E_a^{\ 0}$ for the LSER model, were calculated by fitting, through a multivariable linear regression, the E_a values of the IET process together with the corresponding solvent parameters to Equation 1.[11] By mean of a statistical analysis those coefficients with a low significance level were removed from the calculated model.

In order to guarantee a complete representation of all types of solute/solvent interactions, the selected solvents were taken from the eleven groups of a classification of the most common organic. We tried to make the analysis using the maximum number of solvents possible. To make possible to obtain the experimental value E_a, the diradical **1**, mixed-valence species **1$^{-\bullet}$** and electrolyte have to be soluble in the selected solvent. Then, and related with this first condition, the reduction process has to be effective and relatively fast. On the other hand, in order to get good ESR spectra we took into account the dielectric constants of the solvents, and, as is necessary a big range of temperatures in which the solvent was liquid, the frozen and boiling points of the solvents were also taken into account. Unfortunately, the IET process in the mixed-valence species **1$^{-\bullet}$** was possible to be studied and characterized with only seven solvents. So that, the LSER analysis was realized with the seven values of E_a obtained (see Table S1). Even though we have a few experimental values, we realized different LSER analysis combining the

different solvatochromic parameters and also another analysis using all of them, and the obtained results were always the same. Moreover, the correlation coefficients obtained for every analysis were all between 0.96 and 0.99. Therefore, the analysis is considered as highly robust. The final LSER model described in Table S2 is that which only include the solute/solvent interaction terms that contribute significantly to the E_a changes of the IET process. The LSER model describing the E_a of the mixed-valence species $1^{-\bullet}$ show that E_a is firstly sensitive to changes of the polarity/polarizability variations of the solvent media ($s\pi*$), and secondly, sensitive to changes of the HBD acidity of the solvent media ($a\alpha$). As we thought *a priori*, β and ξ have no influence in the IET process as our mixed-valence species has not any hydrogen atom to form hydrogen bonding with the solvent and is not a basic species.

Table S2. LSER regression coefficients for the mixed valence species $1^{-\bullet}$ describing the solvent-induced thermal electron transfer barrier (ΔG^*).

$n^{[a]}$	*LSER model*$^{[b]}$	Statistics				
		$R^{[c]}$	$s^{[d]}$	$R^2_a{}^{[e]}$	$F^{[f]}$	P
7	$E_a = -2.8(2.2) + 16.0(3.4)\pi* -3.2(1.4)\delta - 15.7(5.8)\alpha$	0.94	1.09	0.84	9.63	0.096

[a] Number of studied solvents. [b] Numbers in parentheses are coefficient standard errors. [c] Coefficient of multiple correlation. [d] Standard error of the estimate. [e] Adjusted coefficient of multiple determination. [f] *F*-test value for derived equation.

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