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Absolute Energies of Interconverting Contact and Solvent-Separated Radical-Ion Pairs

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Supplementary Material.

Determination of the free energies of formation of contact radical-ion pairs from analyses of charge-transfer absorption and emission spectra. The absorption and emission spectra exhibit an approximate mirror image relationship. The spectra were obtained in their "reduced" forms,^{1,2} and tangents taken at the half height values at the low energy side of the absorption band, and at the high energy side of the emission band. The free energy of formation of the CRIP was taken as the average value of the energies at which these tangents intercept the energy axis. For CT spectra, the spectroscopic energies obtained in this way correspond to free energies, rather than enthalpies.¹ Experiments were performed at 22°C. The systems studied, the appropriate electrochemical redox data and the CRIP free energy data are summarized in Table S1. The electrochemical data were obtained as described in ref 3.

References for supplementary material

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Table S1. Free Energies of Formation of Contact Radical-ion Pairs, ΔG_{CRIP} , in Different Solvents, and Electrochemical Redox Potentials of the Acceptors and Donors.

Solvent ^a (ϵ)	Acceptor ^b	Donor ^c	E_{redox}^d (eV)	ΔG_{CRIP}^e (eV)	Δ_{CRIP}^f (eV)
CHX (2.024)	TCB	<i>p</i> -Xy	2.73	3.045	0.315
CHX (2.024)	TCB	HMB	2.26	2.591	0.331
CTC (2.238)	TCB	<i>p</i> -Xy	2.73	2.959	0.229
CTC (2.238)	TCB	TMB	2.59	2.843	0.253
CTC (2.238)	TCB	Dur	2.45	2.689	0.239
CTC (2.238)	TCB	PMB	2.38	2.629	0.249
CTC (2.238)	TCB	HMB	2.26	2.517	0.257
CTC (2.238)	PMDA	<i>p</i> -Xy	2.61	2.878	0.268
CTC (2.238)	PMDA	HMB	2.14	2.397	0.257
CTC (2.238)	DCB	HMB	3.21	3.445	0.235
CTC (2.238)	TCA	HMB	2.03	2.266	0.236
TCE (3.42)	TCA	HMB	2.03	2.201	0.171
TCE (3.42)	TCB	HMB	2.26	2.429	0.169
CHL (4.806)	TCA	HMB	2.03	2.162	0.132
CHL (4.806)	TCB	PMB	2.38	2.449	0.069
CHL (4.806)	TCB	HMB	2.26	2.341	0.081
CHL (4.806)	DCB	HMB	3.21	3.300	0.09
DCM (8.93)	DCB	HMB	3.21	3.276	0.066
DCE (10.37)	TCB	TMB	2.59	2.641	0.051
DCE (10.37)	TCB	HMB	2.26	2.339	0.079
PN (28.8)	DCB	HMB	3.21	3.271	0.061
AN (35.9)	DCB	HMB	3.21	3.248	0.038
AN (35.9)	TCB	<i>p</i> -Xy	2.73	2.746	0.016

^a The solvents are cyclohexane (CHX), carbon tetrachloride (CTC), trichloroethylene, (TCE), chloroform (CHL), dichloromethane (DCM), 1,2-dichloroethane (DCE), propionitrile (PN), and acetonitrile (AN).

^b The acceptors are 1,2,4,5-tetracyanobenzene (TCB), pyromellitic dianhydride (PMDA), 1,4-dicyanobenzene (DCB), and 2,6,9,10-

tetracyanoanthracene (TCA). ^c The donors are *p*-xylene (*p*-Xy), 1,2,4-trimethylbenzene (TMB), durene (Dur), pentamethylbenzene (PMB), and hexamethylbenzene (HMB). ^d E^{redox} is the difference between the oxidation potential of the donor, E^{ox}_{D} , and the reduction potential of the acceptor, $E^{\text{red}}_{\text{A}}$. The reduction potentials, V vs SCE, are: TCB (-0.67), PMDA (-0.55), DCB (-1.62), TCA (-0.44). The oxidation potentials, V vs SCE, are: *p*-Xy (2.06), TMB (1.92), Dur (1.78), PMB (1.71), HMB (1.59). ^e ΔG_{CRIP} is determined from absorption and emission spectra as described above. ^f Δ_{CRIP} is the difference ($\Delta G_{\text{CRIP}} - E^{\text{redox}}$).