Estimation of the solvent reorganization energy and the absolute energy of solvation of charge-transfer states from their emission spectra

Claudia Solís, Viviana Grosso, Nathaniel Faggioli, Gonzalo Cosa, Mario Romero, Carlos Previtali, Hernán Montejano and Carlos Chesta

Supplementary Material

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FIGURES

Figure 1(a)-SI: Temperature effects on the (reduced) emission spectrum of **II** (\sim 1x10⁻⁴ M) in acetonitrile. The emission of the (unquenched) MN fluorophore and that of the CT state are observed at \sim 350 and \sim 230 kJ/mol, respectively. The arrows indicate the effect of the increasing temperature on the position of the exciplex (CT) emission maximum and on the bandwidth of the emission spectra. The spectra are normalized at the CT maximum. Temperatures (from right to left): 282.0, 290.8, 299.5, 308.3, 317.1, 326.0 K. **1(b):** Temperature effects on the (reduced) emission spectrum of **II** in ethyl acetate. Temperatures (from right to left): 282.9, 291.6, 300.1, 308.8, 316.7 and 324, 7 K.



Figure 2-SI: Solvent effect on the (reduced) emission spectrum of **IV** $(1 \times 10^{-4} \text{ M})$ at 298 K. Solvents: (1) c-hexane, (2) butyl ether, (3) ethyl ether, (4) ethyl acetate, (5) butyronitrile and (6) acetonitrile. The spectra were normalized at the spectrum maxima.



Figure 3-SI: Emission spectra of MN (black) and MN / TEA (0.01 M) (dashed) in the vapor phase (T = 433 K). The spectra are normalized at the maxima.



Figure 4-SI: Lippert-Mataga plots for the intermolecular exciplexes and I. CN/TEA (\circ), MN/TEA (\Box), naphthalene / TEA (\blacksquare) and I (\blacktriangle).



TABLES

Medium	$\epsilon^{(a)}$	n ^{2 (b)}	CN / TEA	MN / TEA	Ι	II	III	IV
Vapour phase	1.00	1.00	258 ± 5	$302 \pm 5^{(c)}$	-	-	-	-
n-Hexane	1.88	1.88	237 ± 2	291 ± 1	294 ± 2	-	-	-
c-Hexane	2.02	2.02	237 ± 2	290 ± 1	297 ± 1	318 ± 1	n.o	n.o
TEA	2.42	1.96	224 ± 3	278 ± 1	-	-	-	-
n-Butyl ether	3.08	1.79	220 ± 3	272 ± 1	283 ± 2	295 ± 3	~318 ± 4	n.o.
Ethyl ether	4.34	1.82	209 ± 4	266 ± 2	274 ± 3	280 ± 3	$\sim 304 \pm 4$	n.o.
Ethylacetate	6.02	1.88	n.o. ^(d)	245 ± 3	259 ± 3	263 ± 3	288 ± 3	~316 ± 4
THF	7.58	1.97	n.o.	247 ± 3	259 ± 3	-	283 ± 4	~313 ± 4
Butyronitrile	20.3	1.92	-	-	-	-	273 ± 4	298 ± 4
Propionitrile	28.9	1.87	n.o.	237 ± 4	239 ± 4	-	-	-
Acetonitrile	37.5	1.80	n.o.	235 ± 4	220 ± 4	234 ± 4	262 ± 6	288 ± 4

Table 1-SI: Energy (kJ/mol) of the emission maxima of the CT states (hv_{max}^{ε}) at 298 K in the series of solvents studied.

(a) Static dielectric constant of the medium at 298 K [56]. (b) Optical dielectric constant of the medium at 298 K [56] (c) Energy of the emission maximum in the vapour phase for the naphthalene / TEA exciplex obtained from reference 45 and 46. (d) The emission of the CT state was not observed. d) Extrapolated value, see the main text for details.

Table 2-SI: Singlet-singlet excited state energy (E_{oo}) of the fluorophores, reduction potentials ($E_{red}^{37.5}$), oxidation potentials ($E_{ox}^{37.5}$) and contribution of the A and D to the internal reorganization energy ($\lambda_v = \lambda_{vD} + \lambda_{vA}$).

Compound	E_{oo} / kJ mol ⁻¹	$E_{red}^{37.5}$ (V vs SCE)	$E_{ox}^{37.5}$ (V vs SCE)	λ_{vA} / kJ mol ⁻¹	λ_{vD} / kJ mol ⁻¹
MN	384	-2.54	-	11	-
CN	373	-1.91	-	13	-
TEA	-	-	+1.01, +0.96	-	59
Ι	384	-2.54	$+0.98(-8.96)^{a}$	(11)	(59)
II	384	-2.54	$+0.98(-8.96)^{a}$	(11)	(59)
III	384	-2.54	+1.18 (-9.26) ^a	(11)	(59)
IV	384	-2.54	$+1.42(-9.60)^{a}$	(11)	(59)

a) HOMO level estimated from AM1 semiempirical MO calculations in eV.

Calculation of the enthalpic and entropic contributions to $\Delta G_{-et}^{\varepsilon}, \lambda_s^{\varepsilon}$,

$\Delta G_s^{\mathcal{E}}$ and $\Delta G_s^{n^2}$ from the experimental data.

The enthalpic and entropic contributions were calculated from the experimental parameters A^{ε} and B^{ε} (Table 1 and 2, main text) according to:

a) $\Delta H_{-et}^{\varepsilon} \approx -\frac{1}{2} (A^{n^2} + A^{\varepsilon})$ b) $\Delta S_{-et}^{\varepsilon} \approx \frac{1}{2} (B^{n^2} - B^{\varepsilon})$ c) $\Delta H_{s\lambda}^{\varepsilon} \approx \frac{1}{2} (A^{n^2} - A^{\varepsilon})$ d) $\Delta S_{s\lambda}^{\varepsilon} \approx -\frac{1}{2} (B^{n^2} - B^{\varepsilon})$. c) $\Delta H_s^{\varepsilon} \approx \frac{1}{2} (A^{n^2} + A^{\varepsilon}) - A^{\varepsilon_o}$ e) $\Delta S_s^{\varepsilon} \approx -\frac{1}{2} (B^{n^2} + B^{\varepsilon}) + B^{\varepsilon_o}$ f) $\Delta H_s^{n^2} \approx (A^{n^2} - A^{\varepsilon_o})$; g) $\Delta S_s^{n^2} \approx -(B^{n^2} - B^{\varepsilon_o})$.

Table 3-SI: Estimated enthalpic (kJ/mol) and entropic (J/K mol) contributions to $\Delta G_{-et}^{\varepsilon}$ and λ_s^{ε} for the intermolecular CN / TEA and MN / TEA exciplexes.

		CN /	TEA		MN / TEA				
	ΔG	$\Delta G_{-et}^{\varepsilon}$		$\lambda_s^{\mathcal{E}}$		$\Delta G_{-et}^{\mathcal{E}}$		$\lambda_s^{oldsymbol{arepsilon}}$	
Medium	$\Delta H_{-et}^{\varepsilon}$	$\Delta S_{-et}^{\varepsilon}$	$\Delta H_{\lambda s}^{\varepsilon}$	$\Delta S_{\lambda s}^{\epsilon}$	$\Delta H_{-et}^{\varepsilon}$	$\Delta S_{-et}^{\varepsilon}$	$\Delta H_{\lambda s}^{\varepsilon}$	$\Delta S_{\lambda s}^{\epsilon}$	
Vapour phase	-320 ± 20	42 ± 7	0 ± 0	0 ± 0	-	-	-	-	
n-Hexane	-290 ± 6	106 ± 4	0 ± 2	0 ± 3	-331 ± 5	100 ± 4	0 ± 1	0 ± 4	
c-Hexane	-290 ± 6	106 ± 4	0 ± 2	1 ± 4	-330 ± 5	100 ± 4	0 ± 1	0 ± 4	
Triethylamine	-278 ± 7	123 ± 4	12 ± 3	18 ± 3	-315 ± 5	120 ± 4	16 ± 1	20 ± 4	
n-Butyl ether	-278 ± 7	118 ± 4	12 ± 3	12 ± 3	-314 ± 5	126 ± 4	17 ± 1	26 ± 4	
Ethyl ether	-269 ± 8	129 ± 5	21 ± 4	23 ± 4	-309 ± 5	132 ± 4	22 ± 1	32 ± 4	
Ethyl acetate	-	_	_	-	-298 ± 6	134 ± 4	33 ± 2	34 ± 4	
Tetrahydrofurane	-	_	_	-	-295 ± 6	147 ± 6	36 ± 2	47 ± 6	

]	[II			
	$\Delta G_{-et}^{\mathcal{E}}$		$\lambda_s^{\mathcal{E}}$		$\Delta G_{-et}^{\mathcal{E}}$		$\lambda_s^{arepsilon}$	
Medium	$\Delta H_{-et}^{\varepsilon}$	$\Delta S_{-et}^{\varepsilon}$	$\Delta H_{\lambda s}^{\epsilon}$	$\Delta S_{\lambda s}^{\epsilon}$	$\Delta H_{-et}^{\varepsilon}$	$\Delta S_{-et}^{\varepsilon}$	$\Delta H_{\lambda s}^{\epsilon}$	$\Delta S_{\lambda s}^{\epsilon}$
c-Hexane	-347 ± 5	67 ± 4	0 ± 1	0 ± 1	-367 ± 5	71 ± 1	0 ± 1	0 ± 1
n-Butyl ether	-333 ± 6	92 ± 4	15 ± 2	25 ± 1	-346 ± 6	105 ± 1	22 ± 2	34 ± 1
Ethyl acetate	-314 ± 6	115 ± 6	34 ± 2	48 ± 2	-323 ± 6	126 ± 2	44 ± 2	55 ± 2
Acetonitrile	-287 ± 6	141 ± 6	61 ± 2	74 ± 2	-313 ± 6	111 ± 2	54 ± 2	40 ± 2

Table 4-SI: Estimated enthalpic (kJ/mol) and entropic (J/K mol)	contributions to $\Delta G_{-at}^{\varepsilon}$ and λ	\int_{a}^{ε} for the intramolecular I and II exciplexes.
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Table 5-SI: Estimation of the temperature dependence of the solvatochromic functions f_{ε} and f_{n^2} .

$$f_{x(T)} = \frac{x(T) - 1}{2x(T) + 1}$$
, where $x = \varepsilon$ or n^2 , hence: $\frac{\partial f_{x(T)}}{\partial T} = \frac{3}{(2x(T) + 1)^2} \frac{\partial x(T)}{\partial T}$

Solvent	<i>E</i> (200 K)	$-\partial \varepsilon/\partial T$	$-\partial f_{\varepsilon}/\partial T$	n^2	$-\partial n/\partial T$	$-\partial f_{n^2}/\partial T$	$\partial f_{\varepsilon} / \partial T - \partial f_{n^2} / \partial T$
	(298 K)	x 10 ⁴ K	x 10 ⁴ K	(298 K)	x 10 ⁴ K	$x 10^4 K$	x 10 ⁴ K
c-Hexane	2.02	15.5	1.8	2.02	15.5	1.8	0
Ethyl ether	4.34	200	6.8	1.82	11.7	1.6	4.8
Ethyl acetate	6.02	150	2.6	1.88	12.9	1.7	0.9
THF	7.58	299	3.4	1.97	14.4	1.8	1.7
Acetonitrile	37.5	1600	1.8	1.80	13.3	1.9	-1.1

Electrochemical characterization of compounds II-IV.

It is worth to notice that the reported amine oxidation potentials do not represent the formal values. However, it is known that in these cases the experimental observed E_{ox} (rigorously, $E_{1/2}$) should depart from the standard value by less than 0.06-0.07 V (see for instance: A. J. Bard and L. R. Faulkner, in Electrochemical Methods: Fundamental and Applications, Wiley & Sons, New York, 2nd edn, 2001) introducing a relatively small uncertainty in the calculated free energy changes (which are in the order of 2.8-4.0 eV for BET inspected herein).

	II	III	IV
$E_{1/2 \text{ Fe}}(vs \text{ ps Ag E})^a$	0.465	0.441	0.489
Ep (vs ps Ag E) ^b	0.975	1.161	1.449
E _{1/2 Fe} (<i>vs</i> SCE)	0.46	0.46	0.46
$E_{pC}(vs SCE)^{c}$	0.98	1.18	1.42
ΔE_{pC}	0.00	+0.20	+0.44
HOMO $(calc.)^d$	-8.96	-9.26	-9.60
Δ HOMO (calc.)	0.00	+0.30	+0.64

a) Half wave oxidation potential for ferrocene in acetonitrile *vs*. a pseudo Ag/Ag^+ electrode; b) Half wave oxidation potential for ferrocene in acetonitrile *vs*. SCE; c) Peak oxidation potential of the substrates *vs*. SCE; d) AM1 MO calculated HOMO energies in eV.



A test for equations 9 and 10 (main text) using the data reported by Zimmt et al.

In this section the values of $\Delta G_{-et}^{\varepsilon}$ and λ_s^{ε} calculated using eq. 1 and 2 and 9-10 (main text) using the experimental data reported by Vath, P; Zimmt, M. B., *J. Phys. Chem. A*, **2000**, 104, 2626, are compared.

a) Scheme representing the excitation and emission of the CT ground state complex:

$$(AD) + hv_A^{\mathcal{E}} \to (A^- D^+) \to (AD) + hv^{\mathcal{E}}$$

b) Molecular systems studied by Vath et al.:



c) Experimental values of the absorption $(hv_{A\max}^{\varepsilon})$ and emission maxima $(hv_{\max}^{\varepsilon})$ of the CT states estimated for compounds **a** and **b**, reported by Vath, P; Zimmt, M. B., *J. Phys. Chem. A*, **2000**, 104, 2626. All values are given in kJ/mol.

			(a)			(b)	
	Solvent	$hv_{A\max}^{\mathcal{E}}$	$hv_{\max}^{\mathcal{E}}$	λ_v	$hv_{A\max}^{\varepsilon}$	hv_{\max}^{ε}	λ_{v}
1	2-methylbutane	415.8	315.3	43.4	457.1	346.8	52.1
2	diethyl ether	410.4	280.2	43.4	449.7	278.0	52.1
3	dioxane	408.6	257.9	43.4	451.6	255.2	52.1
4	tetrahydrofurane	409.6	236.1	43.4	447.5	221.3	52.1
5	acetonitrile	410.1	222.2	43.4	453.6	192.1	52.1

d) Equations used for the estimation of $\Delta G_{-et}^{\mathcal{E}}$ and $\lambda_s^{\mathcal{E}}$ from the experimental data in the table above.

$$\Delta G_{-et}^{\varepsilon} = -\frac{1}{2} (h v_{A\max}^{\varepsilon} + h v_{\max}^{\varepsilon})$$
⁽¹⁾

$$\lambda_{s}^{\varepsilon} = \frac{1}{2} \left(h v_{A \max}^{\varepsilon} - h v_{\max}^{\varepsilon} \right) - \lambda_{v}$$
⁽²⁾

$$\Delta G_{-et}^{\varepsilon} \cong -\frac{1}{2} (h v_{\max}^{n^2} + h v_{\max}^{\varepsilon}) - \lambda_{v}$$
(9, main text)
$$\lambda_{s}^{\varepsilon} \cong \frac{1}{2} (h v_{\max}^{n^2} - h v_{\max}^{\varepsilon})$$
(10, main text)

d) Correlation between the values of $\Delta G_{-et}^{\mathcal{E}}$ calculated from equations (1) and (9) for compounds **a** (•) and **b** (°). The numbers between parentheses refer to the solvents as listed in (c).



f) Correlation between the values of λ_s^{ε} calculated from equations (2) and (10) for compounds **a** (•) and **b** (°). The numbers between parentheses refer to the solvents as listed in (c).



Analysis of the values of $\Delta G_{-et}^{\varepsilon_0}$ for the different CT systems

When the values of $\Delta G_{-et}^{\varepsilon}$ estimated for the different exciplexes are compared, some interesting conclusions emerge. For instance, considering that the ionization potential (IP) of the amine donor (TEA) is the same for both intermolecular exciplexes and that they show similar $\mu_e^2/4\pi\varepsilon_o\rho^3$ (and therefore, similar w^{ε_o}), the difference between their extrapolated $\Delta G_{-et}^{\varepsilon_o}$ must reveal the relative *EA* of the electron acceptors. This is, taking into account that:

$$\Delta G_{-et}^{\varepsilon_o} = -IP + EA - w^{\varepsilon_o}$$

thus,

$$\Delta \Delta G_{-et}^{\varepsilon_o}(CN / TEA, MN / TEA) \cong EA(CN) - EA(MN)$$

The value of $\Delta\Delta G_{-et}^{\varepsilon_o}$ calculated using the data on Table 8 is ~ (52 ± 3) kJ/mol, which is in good agreement with the difference estimated from the electronic affinities of MN (0.13 eV¹) and CN (0.68 eV²), ca. ~ 53 kJ/mol.

Similarly, assuming that the ionization potential (IP) and the electronic affinities (EA) of the D and A moieties in compounds I (or in intramolecular MN/TEA exciplex) and II are the same, the difference of the extrapolated $\Delta G_{-et}^{\varepsilon_o}$ (table 8) should reflect the differences between the coulombic attraction terms w^{ε_o} :

$$\Delta\Delta G_{-et}^{\varepsilon_o}(II,I) \cong -w^{\varepsilon_o}(II) + w^{\varepsilon_o}(II)$$

Interestingly, the value of $w^{\varepsilon_o}(II) - w^{\varepsilon_o}(I)$ estimated from the data on Table 8 is ~ (40 ± 5) kJ/mol; which is in very good agreement with the difference (theoretically) calculated by Swinnen *et al.*; *i.e.* 38 kJ/mol.3 The larger w^{ε_o} inferred for **II** is ascribed to the short ethane chain link which does not allow a close contact between the radical ions, thus decreasing the coulombic interactions and destabilizing the CT state. Error! Bookmark not defined.,Error! Bookmark not defined.

On the other hand, taking into account that the **II-IV** show similar $\mu_e^2/4\pi\epsilon_o\rho^3$ (and w^{ϵ_o}) the difference between their $\Delta G_{-et}^{\epsilon_o}$ should mirror the relative IP of the amine donor moieties, *i.e.*:

$$\Delta \Delta G_{-et}^{\varepsilon_o}(II, III \text{ or } IV) \cong -IP(II) + IP(III \text{ or } IV).$$

The values of $\Delta IP(II,III)$ and $\Delta IP(II,IV)$ calculated from the data on Table 8 (main text) are ~ (20 ± 10) and ~(50 ± 10) kJ/mol, respectively. These values are in fair agreement with the difference of theoretical calculated HOMO energies of amine donors: ca. ~29 and ~62 kJ/mol, respectively.

Similarly, the values $\Delta\Delta G_{-et}^{37.5}(II, III \text{ or } IV)$ estimated in acetonitrile from the extrapolated $hv_{\text{max}}^{37.5}$ (table 5) are ~ (30 ± 20) and ~(50 ± 20) kJ/mol, while the free energy changes calculated from the corresponding E_{ox} are ~20 and 44 kJ/mol.

References

^{1 -} Murov, S. L.; Carmicheal, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd. Ed.; Marcel Dekker Inc., New York, 1993.

²⁻ Heinis, T; Chowdhury, S; Kebarle, P., Org. Mass. Spectrom., 1993, 28, 358.

^{3 -} Swinnen, A. M.; Van der Auweraer, M.; De Schryver, F. C. J. Photochem. 1985, 28, 315.