

Solvent effects on the structure of fluorescent 'exciplexes' in rigidly-, flexibly-, and non-bridged donor-acceptor systems

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Abstract- The solvent dependence of the 'exciplex' emission frequency is compared for two electron Donor-Acceptor pairs that are either separate molecular entities, bridged by a flexible trimethylene chain or by a (semi)rigid piperidine ring. It is concluded that in solvents of intermediate and high polarity the emissive state has a structure involving a rather large DA separation in all cases. For the rigidly bridged systems this structure is dictated by the chair conformation of the piperidine ring, for the flexibly bridged systems it implies that in the emissive state the trimethylene chain adopts a (partly) extended conformation and for the non-bridged systems this 'exciplex' structure appears closer to that of a solvent separated ion pair (SSIP) than that of a contact ion pair (CIP). In nonpolar media the exciplex structure for flexibly bridged and non-bridged systems appears to involve a much smaller DA distance, compatible with a folded structure or a CIP.

Under these conditions the rigidly bridged systems either show no exciplex emission at all (in case the charge separated state is thermodynamically inaccessible) or at much higher energies than the flexibly and non-bridged systems. Temperature dependent studies suggest that for flexibly linked systems containing sufficiently strong DA pairs the folded exciplex observed in nonpolar media is formed via a 'harpooning' mechanism involving long-range charge separation followed by electrostatically driven folding.

INTRODUCTION

While the discovery of excited state complexes (exciplexes) has been initiated by that (ref. 1) of excimers, in which two identical molecules are involved, it soon became evident (ref. 2) that this is a more general phenomenon. Especially many examples have since been reported of exciplex formation between a molecule with electron donor (D) and a molecule with electron acceptor (A) properties. For such exciplexes it has been conclusively shown (ref. 3) that their electronic structure can be described by taking into account a large contribution of a configuration in which one electron has been transferred from D to A. In this respect such polar exciplexes thus are closely related to the state reached by excitation of charge-transfer complexes and are in general thought of as contact radical ion pairs (CRIP). While the radical ion pair nature of polar exciplexes has been confirmed extensively via e.g. transient absorption spectroscopy, the distance and relative orientation of the radical ions in the emissive exciplex and especially the eventual solvent dependence of these structural parameters became a topic of early discussion (ref. 4,5). The basic source of the uncertainty about the structure of polar exciplexes is the fact that for those involving powerful D and A species and/or submerged in polar media the energy of the ion pair can be below that of the locally excited states of both D and A irrespective of the DA distance. This contrasts with excimers where the excimer state can only be lowered sufficiently with respect to the first locally excited state to make it the emissive state if extensive electronic interaction (overlap) between the components occurs, thus dictating a close contact structure.

Especially Mataga et al. have provided evidence for an increase with solvent polarity of the average DA distance in the emissive state of polar exciplexes. This evidence relates partly to intermolecular exciplexes (ref. 6) but especially to intramolecular exciplexes formed in systems

$D-(CH_2)_n-A$, where D and A are linked by a flexible polymethylene bridge (ref. 7-11). In a number of the latter systems the exciplex geometry was concluded to change from 'compact' in nonpolar to 'loose' in polar media, thought to correspond to a fully folded and a more or less extended conformation of the polymethylene chain interconnecting D and A.

Studies by us and by others have provided a plethora of D-bridge-A systems in which the bridge is a

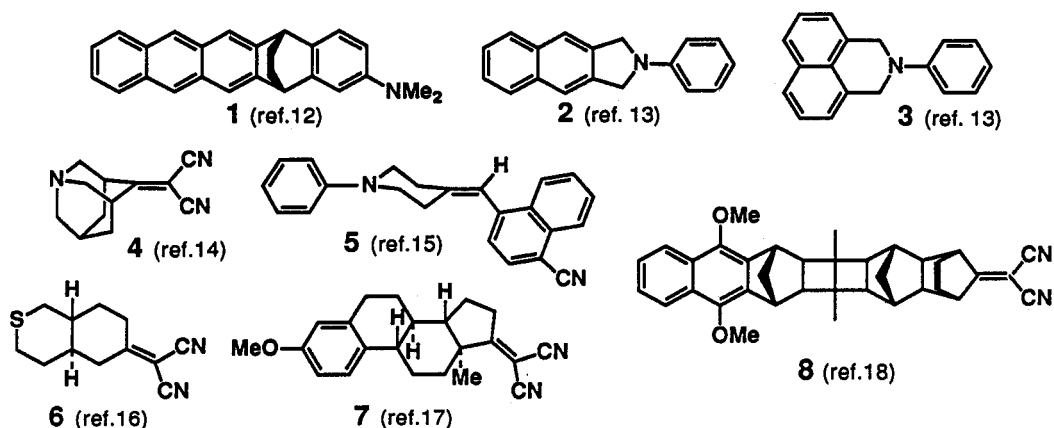


Fig. 1. Selection of rigidly bridged DA systems reported to display intramolecular 'exciplex' emission.

saturated hydrocarbon moiety with a rigidly extended conformation that holds D and A at a distance corresponding to one or more solvent molecule diameters. In many of these systems not only efficient intramolecular photoinduced charge separation has been demonstrated, but also the consecutive charge recombination has occasionally been found to display a radiative component that leads to observation of an unstructured red shifted charge-transfer emission with the strong solvatochromism typical for polar exciplexes (ref. 12-18). Some examples of such rigid systems reported to display 'exciplex' type emission are compiled in Fig. 1. These comprise systems in which the rigid, saturated hydrocarbon bridge has an effective length of two (1, 2, 3), three (4, 5), five (6, 7) and even eight (8) or more (see ref. 18b) carbon-carbon sigma bonds.

In view of these results on rigid systems and the discussion about both intermolecular and flexibly bridged, intramolecular exciplexes we deemed it of interest to compare the emissive behaviour of two typical DA pairs, W and S (see Fig. 2), either unconnected (in W0 and S0), or connected either by a flexible trimethylene chain (in W1 and S1) or by a piperidine ring (in W2 and S2) that severely hampers formation of a conformation with direct DA contact (which would require the piperidine ring to adopt a boat conformation) and restricts the conformational possibilities to those in which D and A are way beyond direct contact. The two DA pairs studied differ only with respect to the strength of the acceptor, which we essentially change from naphthalene (reduction potential $E_{red} = -2.56$ V vs SCE in CH_3CN) in the W(eak) pair to 1-cyanonaphthalene ($E_{red} = -1.96$ V) in the S(strong) pair. While this change has only a minor effect on the energy of the lowest locally excited state, it thus stabilizes the charge separated state by about 0.6 eV in S as compared to W.

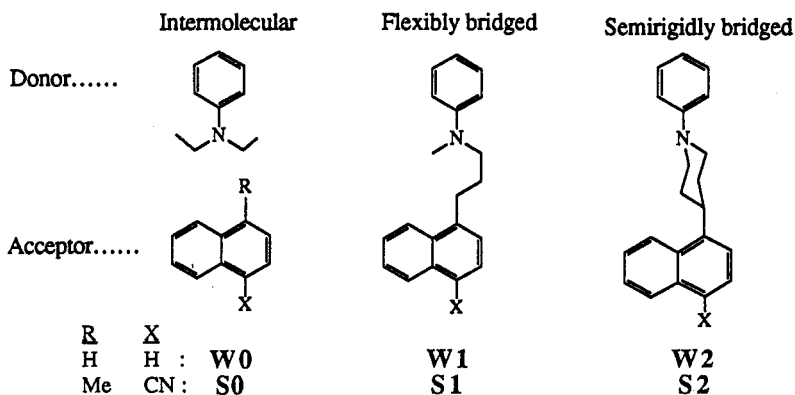


Fig. 2. Structure of the inter- and intramolecular Donor-Acceptor systems investigated.

RESULTS AND DISCUSSION

In Fig. 3 the relative energies of the lowest locally excited (DA^*), CIP (D^+A^-) and SSIP (D^+/A^-) configurations for 'weak'(W) and 'strong'(S) pairs have been indicated in nonpolar and polar media. In a nonpolar medium the level ordering is principally different for S and W pairs. Thus for a W pair only the CIP is thermodynamically accessible via local excitation of either D or A (*case 1*) while for an S pair also the SSIP may become accessible (*case 3*) but will of course still be higher in energy than the CIP because of the Coulombic stabilization of the latter in media of low dielectric constant. In polar media (*case 2*) stron-

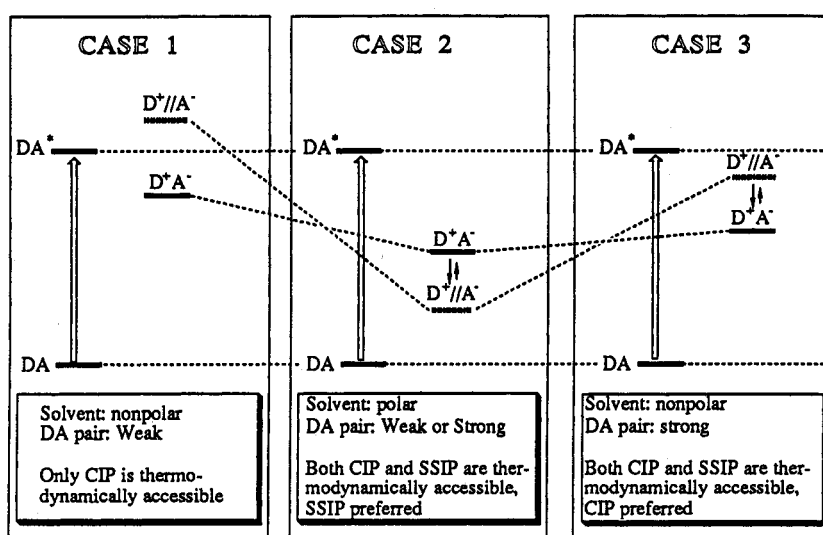


Fig. 3. Schematic energy level diagrams for 'Weak' and 'Strong' DA pairs in nonpolar and polar media

ger solvation of the SSIP and decreased Coulomb stabilization lead to a situation (ref. 19) in which the SSIP is below the CIP and both species are thermodynamically accessible for either S and W pairs. From Fig. 3 it is evident that in *case 1* the CIP is the only species that can be considered as the source of exciplex emission. Also in *case 3* the CIP is the most likely source of such emission unless measures are taken to allow the SSIP to form in high yield via long range electron transfer and to stabilize it against rapid, electrostatically driven, collapse to the CIP. One of the most efficient methods to do so is to connect strong D and A groups to the ends of a rigid molecular bridge that maintains a separation comparable to that found in an SSIP such as is the case in the molecules depicted in Fig. 1 and also in S2. As discussed in the introduction, however, the kinetic interrelation of CIP and SSIP species formed after photoexcitation of DA pairs (either unlinked or linked by polymethylene chains) in polar solvents (i.e. under *case 2* conditions) as well as the nature of the emissive species responsible for the 'exciplex' fluorescence emerging, have been a topic of considerable discussion. The most important aspect of this discussion is whether the electronic and/or geometrical structure of the emissive species could change significantly in response to solvent polarity. We now address this question by comparing the 'exciplex' emission and its solvent dependence for the systems depicted in Fig. 2. Table 1 compiles the position of the 'exciplex' emission maxima (ν_{ct}) measured at room temperature, while in Figs. 4 and 5 we plot these for series W and S as a function of the solvent polarity parameter Δf defined by the solvent dielectric constant (ϵ) and refractive index (n) as: $\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(4n^2 + 2)$.

TABLE 1. Exciplex emission maxima (1000 cm^{-1}) measured at room temperature in various solvents

Solvent	Δf	W0	W1	W2	S0	S1	S2
		ν_{ct}	ν_{ct}	ν_{ct}	ν_{ct}	ν_{ct}	ν_{ct}
n-hexane	0.092	26.18	25.97	a	22.22	22.27	26.32 ^c
cyclohexane	0.100	26.11	25.91	a	22.17	22.22	26.11 ^c
t-decaline	0.110	25.97	25.77	a	22.12	21.12	25.38 ^c
di-n-hexylether	0.170	25.45	25.38	a	21.60	21.55	22.83
di-n-pentylether	0.171	25.38	25.32	a	21.55	21.50	22.57
di-n-butylether	0.194	25.25	25.25	a	21.37	21.46	22.47
di-n-propylether	0.213	25.13	25.06	a	21.28	21.37	21.88
di-i-propylether	0.237	25.00	24.94	25.84	21.14	21.28	21.51
di-ethylether	0.251	24.69	24.63	25.64	20.75	21.01	20.70
n-butylacetate	0.267	24.10	24.15	24.33	20.00	19.72	18.98
ethylacetate	0.292	23.36	23.53	23.15	19.16	19.08	18.18
tetrahydrofuran	0.308	23.20	23.42	22.99	18.98	18.90	18.15
dichloromethane	0.319	22.73	23.09	21.69	18.87	18.90	17.73
ethanol	0.379	21.46	21.10	19.61	b	16.64	b
acetonitrile	0.393	21.28	20.53	19.42	b	15.39	14.84

^a Only local emission observed (around $30,000 \text{ cm}^{-1}$).

^b Local emission strongly quenched but exciplex emission too weak to determine ν_{ct} .

^c Shows a longwavelength shoulder attributed to partial folding of the bridge (ref. 24).

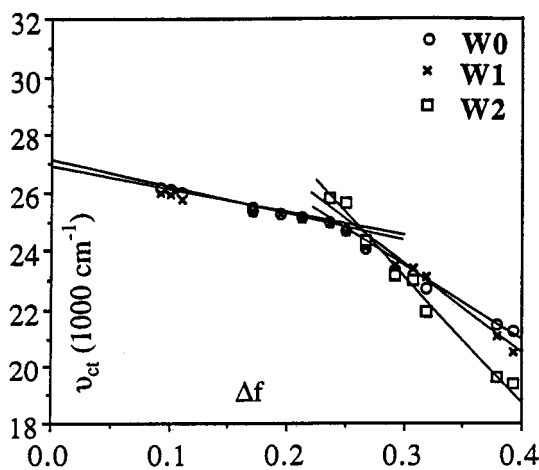


Fig. 4. Exciplex emission frequency (ν_{ct}) as a function of solvent polarity (Δf) for series W.

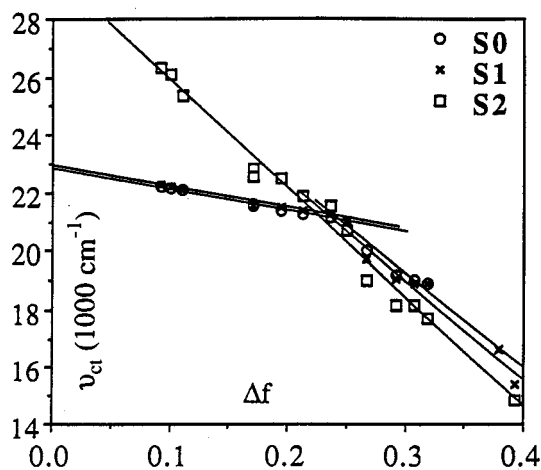


Fig. 5. Exciplex emission frequency (ν_{ct}) as a function of solvent polarity (Δf) for series S.

Assuming that the interaction of the emissive state with the medium can be described as that of a point dipole (magnitude μ) occupying a cavity of radius ρ in a dielectric continuum, and neglecting the dipole moment of the ground state, it can be shown (ref. 20) that the linear relationship defined by eqn (1) should apply, where h is Planck's constant, c the velocity of light and $\nu_{ct}(0)$ the position of the emission maximum in the gasphase:

$$\nu_{ct} = \nu_{ct}(0) - (2\mu^2/hc\rho^3)\Delta f \quad (1)$$

Solvent dependence of exciplex emission for W0, W1 and W2

As evident from Fig. 4, eqn (1) fails to apply over the full range of polarity studied for both W0 and W1, whereas for W2 it can only be tested for $\Delta f \geq 0.237$ since W2 does not display exciplex emission in solvents of lower polarity.

The latter can readily be rationalized if we assume that in W2 the distance between D and A is so large that in nonpolar solvents the charge separated state is located above the locally excited state. In terms of the classification given in Fig. 3 this implies that the charge separated state of W2 behaves like an SSIP for which lowering of the solvent polarity leads to a change from a *case 2* to a *case 1* situation.

That the linear correlation predicted by eqn (1) fails for both W0 and W1 is not without precedent. More or less strong curvature of such plots, invariably with a decrease in slope towards lower solvent polarity, has been noted before especially for flexibly linked systems (ref. 7, 21). It has generally been agreed that such curvature stems from a decrease of the dipole moment of the emissive state in nonpolar solvents. Although it has been suggested (ref. 7) that this could be a result of a decreased DA separation (i.e. a change-over from a 'loose' structure in polar solvents to a 'compact' structure in nonpolar media) it has most generally been attributed but to an increased admixture of locally excited states as the energy gap between these and the charge separated state decreases upon lowering of the solvent polarity. While the latter explanation does not require the occurrence of any major change of the exciplex geometry with solvent polarity, we note that in the polar regime the exciplex emission shown by W0 and W1 is in fact rather close in frequency to that of W2, which has an extended structure involving a large DA distance.

Solvent dependence of exciplex emission for S0, S1 and S2

At first sight the most striking difference with the W series is probably that, in contrast to W2, S2 displays exciplex emission also in nonpolar media. Furthermore application of eqn (1) to the exciplex emission of S2 leads to a satisfactory linear correlation over the complete polarity range. From the slope of the least square regression ($\sim 38000 \text{ cm}^{-1}$) and using $\rho = 6.1 \text{ \AA}$ (40% of the long axis (ref. 20b)) a dipole moment of 29 Debye is calculated. This implies an effective charge separation distance of $\sim 6 \text{ \AA}$, compatible with the extended structure of S2 in the ground state being retained in the emissive 'exciplex'.

Even more remarkable perhaps is that, if we neglect the low polarity region, the position of the exciplex emission and especially its solvent dependence for S0 and S1 are quite similar to those for S2. This similarity seems even more pronounced than in the case of the W series. We feel that this can only imply that in more polar media also for S0 and S1 the exciplex emission observed stems largely or even exclusively from a dipolar state with a very large DA separation comparable to that in S2. For S1 this requires a partly or perhaps even fully extended conformation of the trimethylene bridge and for S0 it is more compatible with an SSIP than with a CIP structure.

While the exciplex emission frequency of S2 correlates linearly with Δf over the whole polarity region,

implying a solvent independent value of μ for this semirigidly bridged system, the dipole moment of the emissive state appears to diminish considerably for both **S0** and **S1** in nonpolar media analogous to what was found for **W0** and **W1** (see above). As we discussed there, a smaller dipole moment can either arise from a reduction in DA distance or from a decreased degree of charge separation due to the admixture of locally excited states. The effect of the latter, however, is expected to be strongly reduced in the **S** series as compared to the **W** series since the energy of the charge separated state in **S** is lowered by about 0.6 eV with respect to that in the **W**, while the energy of the lowest locally excited state is only marginally affected (in the gasphase $E_{00} = 3.93$ eV (ref. 22) for the naphthalene and 3.87 eV (ref. 23) for the 1-cyano-naphthalene chromophore). Because in both series the change in dipole moment for the emissive state of the intermolecular and the flexibly linked systems as a function of the solvent polarity appears virtually identical (compare Figs. 4 and 5) we now conclude that it must be mainly due to a change in the effective DA distance. Thus, while the 'exciplex' emission shown by **S1** and **S0** (as well as by **W0** and **W1**) stems from an extended or SSIP-like structure in the polar regime, this changes over to a more folded or CIP-like structure in the nonpolar regime. The change of structure appears to occur over a rather narrowly defined polarity region, judging from the fact that the $\Delta f/v_{ct}$ dependence for **S0** and **S1** (as well as for **W0** and **W1**) can be fit quite well in terms of two discrete linear regions (see Figs. 4 and 5). In this context it is important to note that the change-over between these two regions occurs at the same polarity for the **W** and the **S** series and close to where an inversion is predicted (ref. 19) between the energies of the CIP and the SSIP. A *caveat* regarding the comparison of v_{ct} values in polar media is in place here, because, as has been pointed out before (ref. 9, 11), in such media the sensitivity of this parameter towards changes in DA distance tends to become rather small. This is especially so for SSIP like structures, for which eqn (1) cannot be expected to be adequate.

Temperature dependence of the exciplex emission for **W1** and **S1** in nonpolar media

Figs. 6 and 7 show the influence of lowering the temperature on the emissive behaviour of **W1** and **S1** in methylcyclohexane. For **W1** the exciplex emission disappears upon cooling and at the same time emission typical for the locally excited state of either D or A develops in the 330 nm region. This behaviour is common for flexibly linked bichromophores incorporating rather weak DA pairs as well as for intramolecular excimers and is readily rationalized in terms of a *case 1* (see Fig. 3) situation. Thus, assuming that the most stable ground state conformation is an extended one with a DA separation similar to that in an SSIP, it is evident that restriction of the thermal mobility of the trimethylene chain by cooling will effectively prohibit formation of a charge separated state.

The behaviour of **S1** is quite different. While cooling abolishes the exciplex emission in the 450 nm region, attributed to an exciplex with close DA contact similar to that found in a CIP, no emission typical for the locally excited state of either D or A (ca. 337 nm) arises. Instead a new, slightly structured, emission appears around 370 nm, which is close to the position of the emission shown by **S2** in nonpolar media (see Table 1) at room temperature and attributed to a charge separated state with a large DA distance similar to that found in an SSIP. This implies not only that the level ordering in **S1** corresponds to *case 3* (see Fig. 3) but also that the formation of the CIP type exciplex emitting at 450 nm in nonpolar media is probably preceded by formation of an SSIP type structure, as recently confirmed by time resolved measurements (ref. 24). In polar media the latter is also responsible for the 'exciplex' emission observed at room temperature, but in nonpolar media the electrostatic attraction rapidly transforms it to the CIP at room temperature. We have shown before (ref. 22, 23, 25, 26) that in the gasphase and in nonpolar media this 'harpooning' mechanism is a viable route towards formation of close contact intramolecular exciplexes in D-bridge-A systems involving other semiflexible bridges and a sufficiently strong DA pair, and the present results for **S1** prove

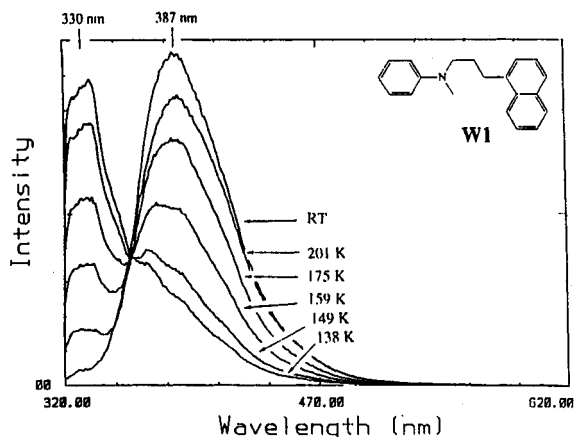


Fig. 6. Fluorescence of **W1** in methylcyclohexane as a function of temperature (excitation at 300 nm).

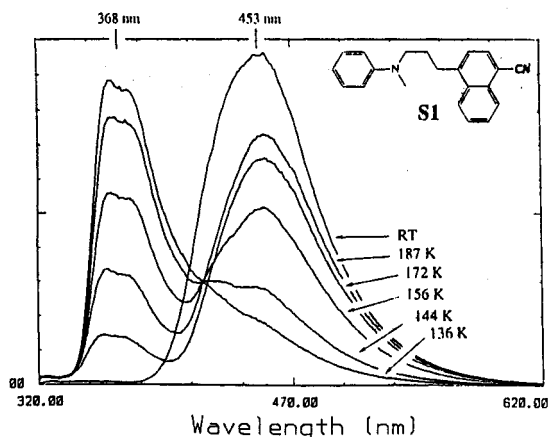


Fig. 7. Fluorescence of **S1** in methylcyclohexane as a function of temperature (excitation at 300 nm).

that this is also true for simple polymethylene bridges. The interesting observation that the emission of the extended exciplex of S1 in nonpolar media at low temperature shows a slight structure (see Fig. 7), possibly indicative for admixture of locally excited state character, deserves further investigation.

Concluding remarks

The present results on series S and W extend our preliminary report (ref. 27) on W1 and W2 and appear to substantiate long standing proposals (4, 6-11) that the structure of emissive polar exciplexes formed between separate or flexibly bridged D and A species may change considerably in response to solvent polarity, from a contact ion-pair (CIP)-type structure in nonpolar to a more solvent separated ion pair (SSIP)-type structure in polar media. Furthermore the CIP-like intramolecular exciplex formed in nonpolar media by a flexibly linked D-(CH₂)₃-A system incorporating a strong DA pair (S1) appears to have an extended SSIP-like precursor.

Acknowledgements

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REFERENCES

1. Th. Förster and K. Kasper, *Z. f. Phys. Chem. Neue Folge* **1**, 275 (1954).
2. H. Leonhardt and A. Weller, *Ber. Bunsenges. Physik. Chem.* **67**, 791 (1963).
3. H. Beens and A. Weller, *Acta Phys. Polon.* **34**, 593 (1968).
4. N. Mataga, T. Okada, and N. Yamamoto, *Bull. Chem. Soc. Japan* **39**, 2562 (1966) and *Chem. Phys. Lett.* **2**, 397 (1967).
5. H. Knibbe, K. Röllig, F.P. Schäfer, and A. Weller, *J. Chem. Phys.* **47**, 1184 (1967).
6. N. Mataga and Y. Murata, *J. Am. Chem. Soc.* **91**, 3144 (1969).
7. S. Masaki, T. Okada, N. Mataga, Y. Sakata and S. Misumi, *Bull. Chem. Soc. Japan* **49**, 1277 (1976).
8. N. Mataga, T. Okada, H. Masuhara, N. Nakashima, Y. Sakata and S. Misumi, *J. Lumin.* **12/13**, 159 (1976).
9. T. Okada, T. Saito, N. Mataga, Y. Sakata and S. Misumi, *Bull. Chem. Soc. Japan* **50**, 331 (1977).
10. T. Okada, M. Migita, N. Mataga, Y. Sakata and S. Misumi, *J. Am. Chem. Soc.* **103**, 4715 (1981).
11. K. Nakatani, T. Okada, N. Mataga and F.C. De Schryver, *Chem. Phys.* **121**, 87 (1988).
12. M.R. Wasielewski, D.W. Minsek, M.P. Niemczyk, W.A. Svec and N.C. Yang, *J. Am. Chem. Soc.* **112**, 2823 (1990).
13. W. Rettig, R. Haag and J. Wirz, *Chem. Phys. Lett.* **180**, 216 (1991).
14. A.W.J.D. Dekkers, J.W. Verhoeven and W.N. Speckamp, *Tetrahedron* **29**, 1691 (1973).
15. a) G.F. Mes, B. de Jong, H.J. van Ramesdonk, J.W. Verhoeven, J.M. Warman, M.P. de Haas and L.E.W. Horsman-van den Dool, *J. Am. Chem. Soc.* **106**, 6524 (1984); b) R.M. Hermant, N.A.C. Bakker, T. Scherer, B. Krijnen and J.W. Verhoeven, *J. Am. Chem. Soc.* **112**, 1214 (1990).
16. P.Pasman, F.Rob and J.W. Verhoeven, *J. Am. Chem. Soc.* **104**, 5127 (1982).
17. a) P. Pasman, N.W. Koper and J.W. Verhoeven, *Recl. Trav. Chim. Pays-Bas* **101**, 363 (1982); b) P. Pasman, G.F. Mes, N.W. Koper and J.W. Verhoeven, *J. Am. Chem. Soc.* **107**, 5839 (1985).
18. a) H. Oevering, M.N. Paddon-Row, M. Heppener, A.M. Oliver, E. Cotsaris, J.W. Verhoeven and N.S. Hush, *J. Am. Chem. Soc.* **109**, 3258 (1987); b) H. Oevering, J.W. Verhoeven, M.N. Paddon-Row and J.M. Warman, *Tetrahedron* **45**, 4751 (1989); c) A.M. Oliver, M.N. Paddon-Row, J. Kroon and J.W. Verhoeven, *Chem. Phys. Lett.* **191**, 371 (1992).
19. A. Weller, *Z. f. Phys. Chem. Neue Folge* **133**, 93 (1982).
20. a) E. Lippert, *Z. Naturforsch.* **10A**, 541 (1955); b) E. Lippert, *Z. Electrochem., Ber. Bunsenges. Physik. Chem.* **61**, 962 (1957).
21. A.M. Swinnen, M. van der Auweraer, F.C. De Schryver, C. Windels, R. Goedeweck, A. Vannerem and F. Meeus, *Chem. Phys. Lett.* **95**, 467 (1983).
22. R.M. Hermant, B. Wegewijs, J.W. Verhoeven, A.G.M. Kunst and R.P.H. Rettschnick, *Recl. Trav. Chim. Pays-Bas* **107**, 349 (1988).
23. B. Wegewijs, R.M. Hermant, J.W. Verhoeven, A.G.M. Kunst and R.P.H. Rettschnick, *Chem. Phys. Lett.* **140**, 587 (1987).
24. T. Scherer and J.W. Verhoeven, to be published.
25. B. Wegewijs, R.M. Hermant, J.W. Verhoeven, M.P. de Haas and J.M. Warman, *Chem. Phys. Lett.* **168**, 185 - 190 (1990).
26. J.W. Verhoeven, *Pure & Appl. Chem.* **62**, 1585 (1990).
27. T. Scherer, R.J. Willemse and J.W. Verhoeven, *Recl. Trav. Chim. Pays-Bas* **110**, 95 (1991).