Supporting Information

EPR Spectroscopy of Bis(triarylamine) Paracyclophanes as Model Compounds for the Intermolecular Charge-Transfer in Solid State Materials for Optoelectronic Applications

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Table S1. Redox potentials and structural characteristics of compounds **I-IX**. $E_{1/2}$ are the half-wave potentials measured by cyclic voltammetry in CH_2Cl_2 vs. ferrocene/ferrocenium (0.15 M tetrabutylammonium hexafluorophosphate); error ±5 mV. r_{N-N} is the nitrogen-nitrogen distance determined by AM1 computations and the minimal number of bonds interconnecting the centres is reported. The redox properties have been taken from the quoted literature.

Compound	r_{N-N} / Å	no. bonds	$E_{1/2}$(I) / mV	$E_{1/2}$(II) / mV	ΔE / mV	Lit.
I	15	16	200	250	50	[1]
II	19.9	20	240	290	50	[1]
III	25	24	290	340	50	[1]
IV	19.9	21	240	280	40	this work
V	19.3	17	270	320	50	[1]
VI	19.3	17	275	335	60	[2]
VII	28.7	25	330	385	55	[3]
VIII			290			this work
IX			270			[1]

Optical Characterization of II[+] and IV[+]

The data of **II[+]** deviate from those in ref.[1] because the reduced (ε/ν) absorption spectrum was used for the analysis in this paper. Data evaluation, AM1 computations and notation follows those in ref.[1].

Table S2. Experimental data obtained from Vis/NIR spectra recorded in CH_2Cl_2 and spectra decomposition by Gaussian functions.

	$\tilde{\nu}_a{}^a$ / cm^{-1}	$\Delta\tilde{\nu}_{1/2}{}^b$ / cm^{-1}	ε^c / M^{-1} cm^{-1}	μ_{ga} / D	$\tilde{\nu}_b{}^a$ / cm^{-1}	$\Delta\tilde{\nu}_{1/2}{}^b$ / cm^{-1}	ε^c / M^{-1} cm^{-1}	μ_{gb} / D	$\tilde{\nu}_{\pi-\pi^*}{}^a$ / cm^{-1}	ε^c / cm^{-1}
II⁺	5870	4820	1700	3.5±0.2	10730	2280	18300	6.2±0.3	13460	28700
IV⁺	8500	5550	860	2.3	10610	2600	13820	5.8	13500	23720

^{a} ±200 cm^{-1}. ^{b} ±200 cm^{-1}. ^{c} ±5%.

All semiempirical calculations were done using the AM1 parameterization implemented in the MOPAC97 program.[4] All optimization were performed without symmetry restrictions in Cartesian coordinates by the eigenvector following (EF) routine. The configuration interaction included singles and doubles excitations (CISD) within an active orbital window consisting of the four highest doubly occupied, one singly occupied and the two lowest unoccupied orbitals. *Pulay*'s procedure was used as the self consistent field (SCF) converger of all calculations. The effect of the solvent (CH_2Cl_2) was simulated using the conductor-like screening model (COSMO) including the parameters $\varepsilon = 2.0$ and a radius of the solvent of 2.5 Å at the CISD optimized gas phase structures. The experimental permittivity of CH_2Cl_2 is 8.9 but a previous study revealed that a smaller empirical permittivity yields more reliable results.

Table S3. AM1-CISD and AM1-CISD+COSMO ($\varepsilon = 2$) computed and experimental adiabatic dipole moment differences and transition moments and diabatic dipole moment differences calculated by GMH three-state model in D.

		$\mu_{gg}-\mu_{gg}$	$\mu_{aa}-\mu_{gg}$	$\mu_{bb}-\mu_{gg}$	μ_{ga}	μ_{gb}	μ_{ab}	$\mu_{11}-\mu_{11}$	$\mu_{22}-\mu_{11}$	$\mu_{33}-\mu_{11}$
II+	AM1-CISD[a]	0	69.2	21.2	22.2	6.3	12.7	0	85.8	24.8
	+ COSMO[a]	0	66.0	30.8	6.5	8.9	7.1	0	71.1	33.8
	exp.[a, c]	-	-	-	3.5	6.2	-	0	69.0	31.7
IV+	AM1-CISD[b]	0	70.7	36.7	27.6	4.4	12.3	0	93.4	46.7
	+ COSMO[b]	0	61.0	43.5	3.9	6.8	8.4	0	65.9	43.2
	exp.[b, c]	-	-	-	2.3	5.8	-	0	65.3	42.0

[a] Odd number of positive off-diagonal transition moments. [b] Even number of positive off-diagonal transition moments [c] For the three-level GMH analysis the experimental values and, where lacking, the COSMO ($\varepsilon = 2.0$) values were used.

Table S4. Transition energies (AM1-CISD and AM1-CISD+COSMO computed and experimental) and diabatic electronic couplings (GMH) in cm^{-1}. We stress that in case of **IV+** the electronic couplings are highly sensitive to the choice of transition energies because of the close proximity of IV-CT and bridge band energies.

		$\tilde{\nu}_a$	$\tilde{\nu}_b$	$V_{12}{}^a$	$V_{13}{}^a$	$V_{23}{}^a$	$V_{\text{two-state}}{}^b$
II+	AM1-CISD[d]	8640	11310	2380	480	540	2330
	+ COSMO[d]	10030	13060	1320	2850	340	970
	exp.[d, f]	5870	10730	580	1850	860	310
IV+	AM1-CISD[c]	9060	12490	2370	2540	1360	2790
	+ COSMO[d]	12660	11790	270	2150	250	800
	exp.[d, e]	8500	10610	110	1530	720	320

[a] Obtained by the GMH three-state model. [b] Obtained by the GMH two-state model. [c] Even number of positive coupling values. [d] Odd number of positive coupling values. [e] For the three-level GMH analysis the experimental values and, where lacking, the COSMO (in the solvent) values were used.

The three-state-GMH-PES fit yields the following parameters for **II$^+$**

λ_1=6500 cm^{-1}, λ_2=3200 cm^{-1}, ΔG_B=6800 cm^{-1}, C=0.18, ΔG^*=1060 cm^{-1}; $\Delta G^*_{\text{two-state}}$=1170 cm^{-1}
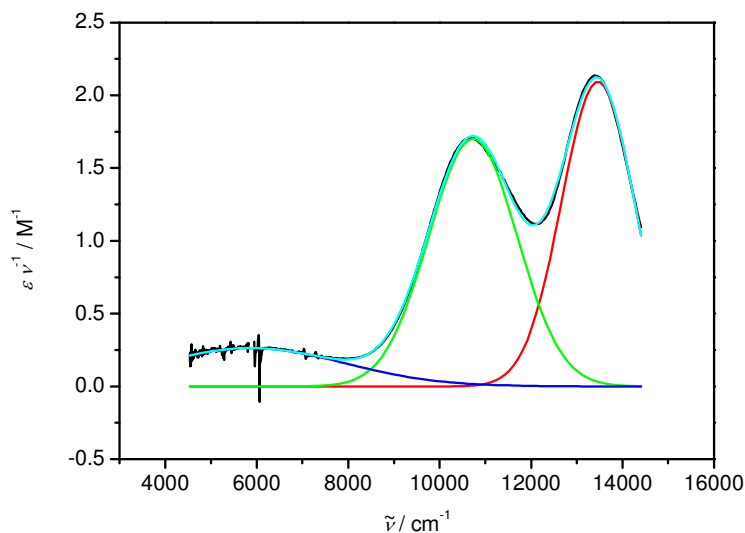

Figure S1. Reduced absorption spectrum (black line) of **II$^+$** in MC and decomposition into three Gaussians and the sum of those (cyan line).

The three-state-GMH-PES fit yields the following parameters for **IV$^+$**

λ_1=8500 cm^{-1}, λ_2=4500 cm^{-1}, ΔG_B=5500 cm^{-1} C=0, ΔG^*=2000 cm^{-1}; $\Delta G^*_{\text{two-state}}$=1730 cm^{-1}
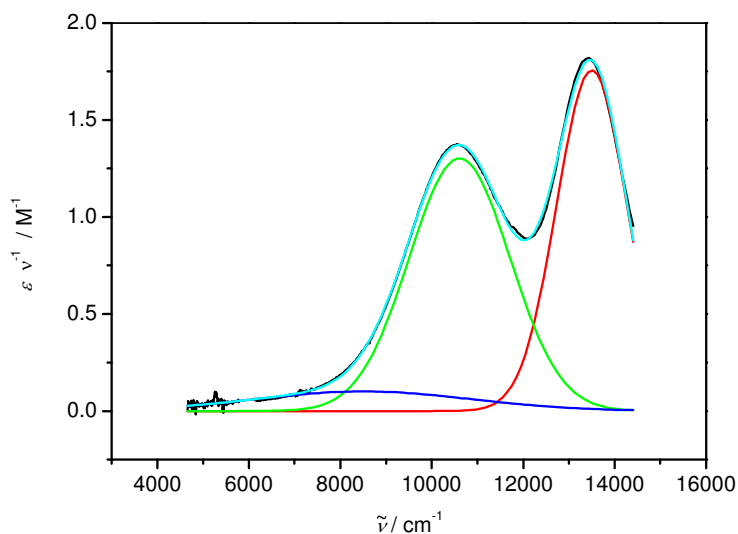

Figure S2. Reduced absorption spectrum (black line) of **IV$^+$** in MC and decomposition into three Gaussians and the sum of those (cyan line).

(1)   Amthor, S.; Lambert, C. *J. Phys. Chem. A* **2006**, *110*, 1177-1189.
(2)   Lambert, C.; Nöll, G. *J. Am. Chem. Soc.* **1999**, *121*, 8434-8442.
(3)   Heckmann, A.; Lambert, C.; Amthor, S. *Chem. Commun.* **2006**, 2959-2961.
(4)   Stewart, J. J. P. *MOPAC97*; Fujitsu Limited, 1997