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Electronic Supplementary Informations

Solvent-tuned Dual Emission: a Structural and Electronic Interplay highlighting a novel Planar ICT (OPICT)

Sylviane CHEVREUX, Romain PAULINO NETO, Clémence ALLAIN, Keitaro NAKATANI, Patrice JACQUES, Ilaria CIOFINI, Gilles LEMERCIER

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Experimental and Computational Details

Absorption spectra were recorded on a Varian Cary 5000 and a Shimadzu UV-2401PC spectrophotometers. Emission and excitation spectra were recorded on a Varian Cary Eclipse fluorimeter at concentrations around $10^{-6} – 10^{-5}$ mol/L.

Quantum yield Φ were determined at 25 °C in a deoxygenated solution using quinine sulfate in H_2SO_4 0.1M as reference ($\Phi = 0.54$, *J. Phys. Chem.,* **1961***, 65,* 229) and following formula: $\Phi_X = \Phi_{ref}*(Grad_X/Grad_{ref})*((n_X)^2/(n_{ref})^2)$, with the subscripts "X" referring to PhenPENMe$_2$ and "ref" to quinine sulfate in H_2SO_4 0.1 M; Φ the quantum yield; Grad the gradient from the plot of emission intensity area vs absorbance and n the refractive index of the solvent. Quantum yields of ICT and LE were determined after irradiation at 380 and 340 nm, on deconvoluted spectra for this last one to discriminate ICT and LE quantum yields.

The fluorescence decay curves were obtained with the time-correlated single-photon-counting method using a Spectra-Physics titanium-sapphire Tsunami laser pumped by a Millennia Xs laser (82 MHz, repetition rate lowered to 4 MHz thanks to a pulse-picker, around 500 fs pulse width, a doubling and a tripling crystal are used to reach 330 nm excitation). Fluorescence photons are detected at 90°, through a monochromator, with a Hamamatsu MCP photomultiplier R3809U. The data were acquired using a SPC-630 TCSPC system (Becker & Hickl GmbH). The analysis is performed with the Globals software from Laboratory for Fluorescence Dynamics (LFD).

All calculations were performed using the Gaussian software, in its 09 version[1]. The basis set used for all atoms for both structural optimizations and excited states (TD-DFT) calculations was the 6-311+G**. Solvent effects (here DMSO) were taken into account by means of the polarizable continuum model (PCM[2]) using the conductor-like PCM model (CPCM) as implemented in the Gaussian package[3]. The PBE0 functional[4] was used throughout. Additional calculations were also performed using the CAM-B3LYP functional, in order to confirm the nature of the excited states. Since no qualitative change was observed, only PBE0 results will be discussed.

References

1- Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.
2- Miertuš S., Scrocco E., Tomasi J.; *Chem. Phys.* **1981**, *55*, 117
3- Barone V., Cossi M.; *J. Phys. Chem. A* **1998**, *102*, 1995
4- Adamo C., Barone V., *J. Chem. Phys.* **1999**, *110*, 6158.

Figure S1: UV-vis spectra in several solvents of **Phen-PENMe$_2$**.

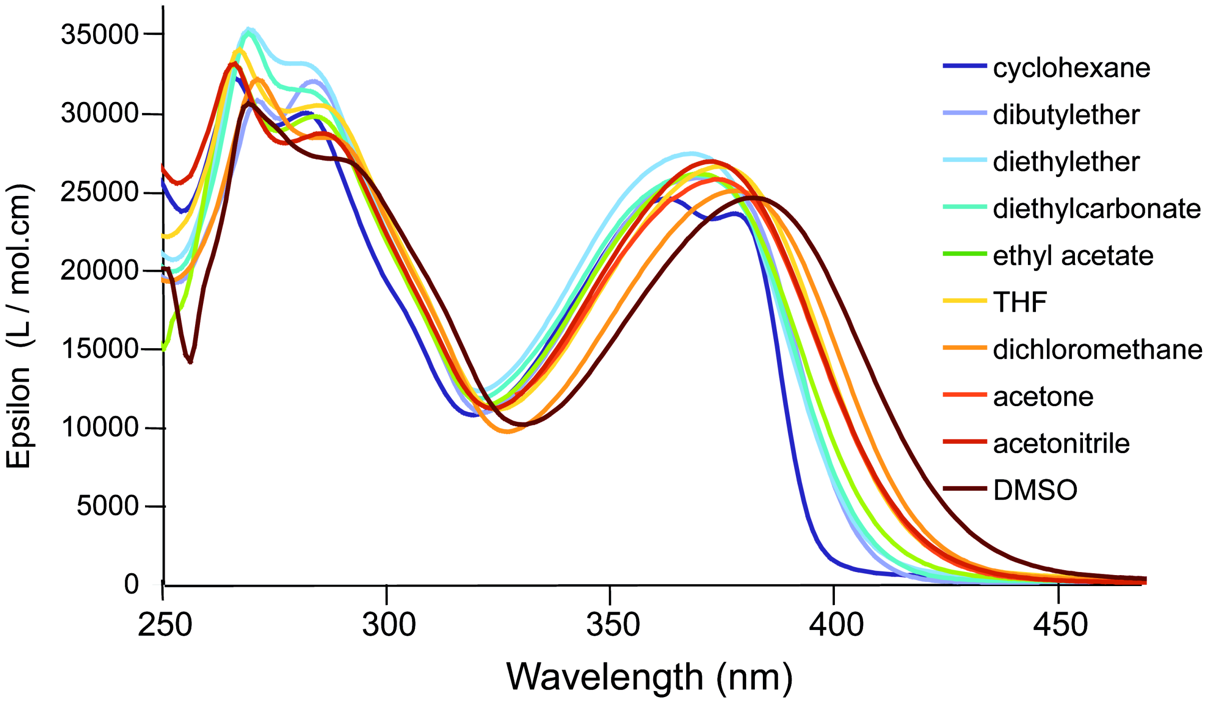


Figure S2. Normalized emission spectra of **Phen-PENMe$_2$** in aprotic solvents upon 380 nm excitation.

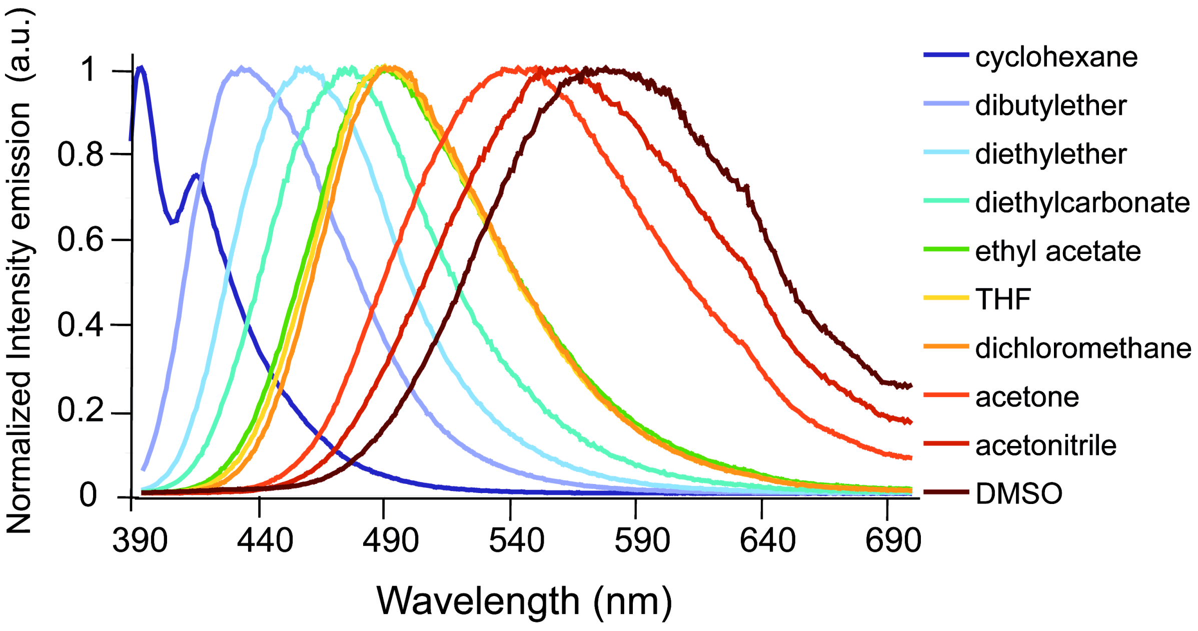


Figure S3. Normalized emission spectra of **Phen-PENMe$_2$** in aprotic solvents upon 340 nm excitation.

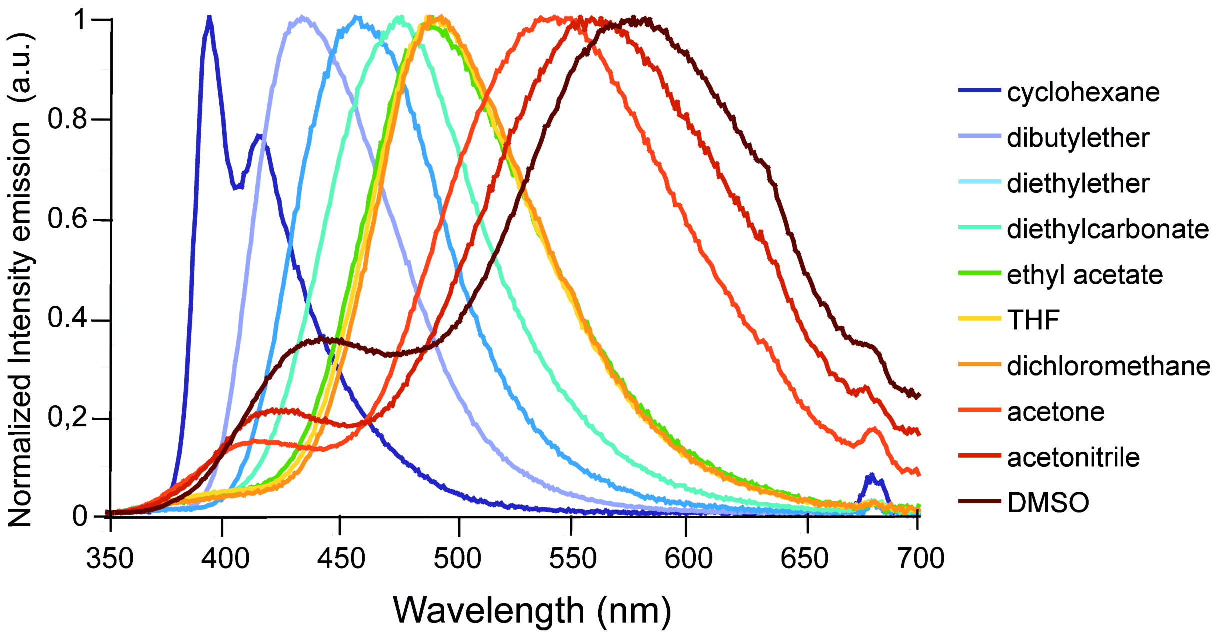


Figure S4. Emission spectra of **Phen-PENMe₂** in several mixtures of CH_3CN/DMSO upon an excitation at 340 nm.

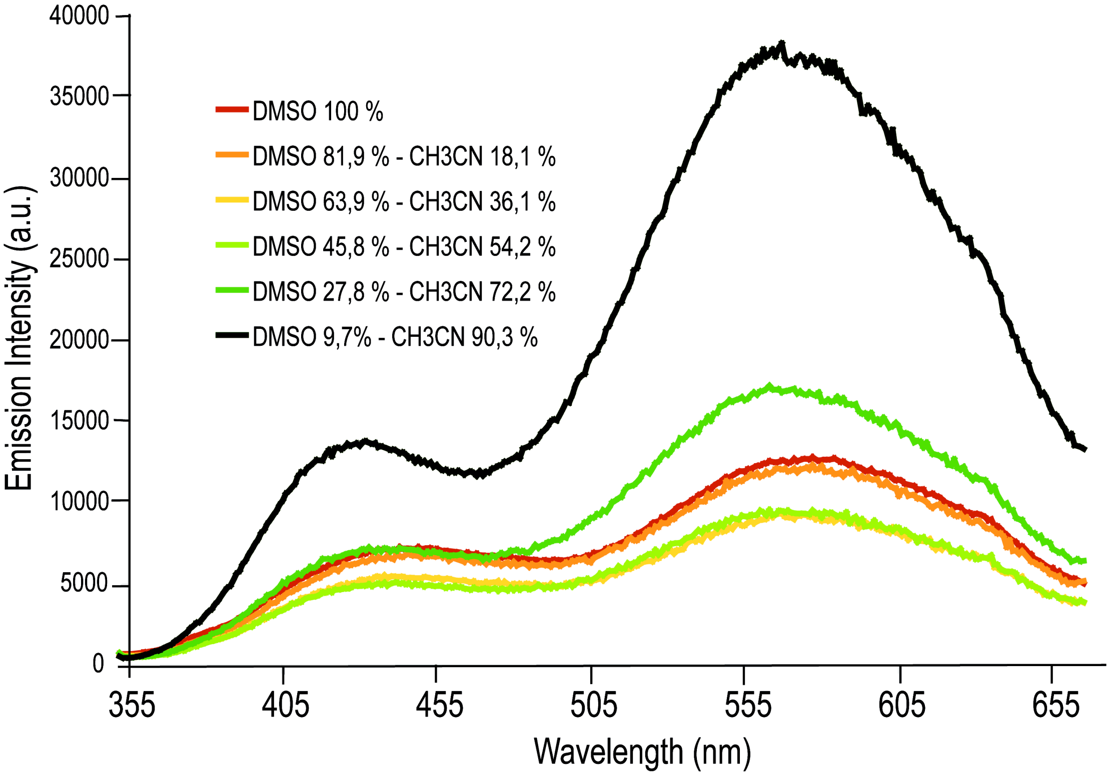


Table S1

Vertical excited states computed at the most stable ground state conformation, *i.e*. planar (ϕ=0°), obtained at PBE0 level.

Excited State	E(eV)	λ(nm)	f (a.u.)	Main Transition	Main Character
1	2.96	419	0.9258	HOMO/LUMO	ICT
2	3.19	388	0.0540	HOMO/LUMO+1	ICT
3	3.99	310	0.5626	HOMO/LUMO+2	ICT
4	4.17	298	0.0529	HOMO-1/LUMO	π-π*
5	4.19	296	0.0402	HOMO-1/LUMO+1	ICT
6	4.21	295	0.0529	HOMO/LUMO+3	ICT
7	4.25	292	0.0012	HOMO-3/LUMO	n-π*
8	4.29	289	0.0008	HOMO-3/LUMO+1	n-π*
9	4.53	274	0.2495	HOMO/LUMO+4	ICT
10	4.71	263	0.0008	HOMO-5/LUMO	n-π*
11	4.71	263	0.1486	HOMO/LUMO+4	ICT
12	4.78	259	0.0022	HOMO-7/LUMO	n-π*
13	4.82	257	0.5277	HOMO-2/LUMO+1	LE (π-π*)
14	4.84	256	0.0013	HOMO-5/LUMO+1	n-π*
15	4.86	255	0.0202	HOMO/LUMO+5	ICT

Table S2 : Quantum yield (measured in intensity) of **Phen-PENMe$_2$** in acetonitrile (ACN), DMSO and an acetonitrile/DMSO mixture (excitation wavelength 330 nm)

Solvents	Emission	Q.Y. (%)	Lifetime (s)	k_r	k_{nr}	k_r/k_{nr}
ACN	LE	0.02	1.82E-09	1.10E+07	5.38E+08	0.02
	ICT	0.09	4.32E-09	2.08E+07	2.11E+08	0.10
	ICT[1]	0.08	4.34E-09	1.84E+07	2.14E+08	0.09
55% ACN - 45% DMSO	LE	0.03	1.95E-09	1.54E+07	4.97E+08	0.03
	ICT	0.07	4.49E-09	1.56E+07	2.07E+08	0.07
	ICT[1]	0.05	4.50E-09	1.11E+07	2.11E+08	0.05
DMSO	LE	0.02	1.99E-09[2]	1.01E+07	4.92E+08	0.02
	ICT	0.03	4.59E-09[2]	6.54E+06	2.11E+08	0.03
	ICT[1,2]	0.04	4.62E-09[2]	8.66E+06	2.08E+08	0.04

[1] Excitation at 380 nm ; [2] 95%DMSO 5% CH_3CN.

Table S3 : Computed (PBE0, in DMSO) emission energy associated to the lowest ICT and π-π^* emissive excited states.

State	E(eV)	λ(nm)	f (a.u.)	Main Transition	Main Character
1[a]	2.52	492	1.36	HOMO/LUMO	ICT
2[a]	2.79	445	0.11	HOMO/LUMO+1	ICT
3[b]	3.28	378	0.96	HOMO-1/LUMO	π-π^*

[a] Starting from a planar conformation (φ = 0°).[b] starting from an orthogonal conformation (φ = 90°).

Lippert-Mataga equation establishes the relationship between the Stokes' shift $\Delta\nu_{ST}$ and the solvent polarity; it can be used, to estimate the variation (μ_{CT} - μ_g), in the dipole moment between the ground and the excited states.

$$\Delta\nu_{ST} = \Delta\nu^0{}_{ST} + \left[\frac{2}{(4\pi\varepsilon_0)(hca^3)}\right] \times (\mu_{CT} - \mu_g)^2 \times \Delta f(\varepsilon,n). \qquad (1)$$

a being the value of the Onsager cavity radius in which the fluorophores resides, *h* the Planck's constant, c the celerity of light, ε_0 the vacuum permittivity, and Δf(ε,n) defined by:

$$\Delta f(\varepsilon,n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \qquad (2)$$

With ε being the static dielectric constant and n the refractive index of the solvent.

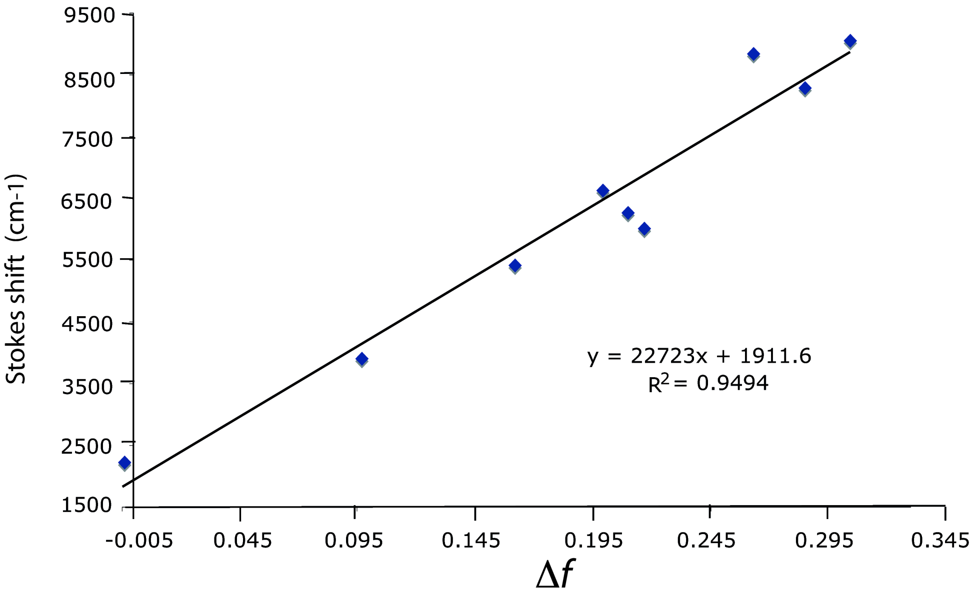
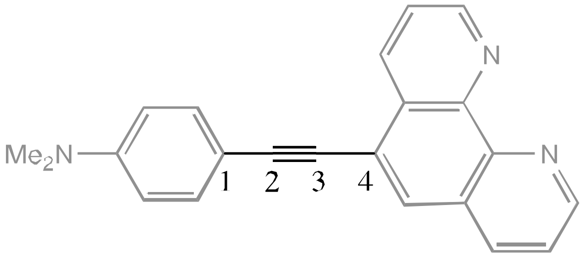


Figure S5 : Plot of the Stokes's shift against the Lippert-Mataga polarity parameter Δf according to equation (1) for compound **Phen-PENMe₂** in several aprotic solvents (slope around 23000 cm^{-1}, and $R^2 = 0.95$).

5.6 Å has been calculated for the Onsager *radius*, then the difference between excited-state and fundamental state dipolar moment value was estimated (with an experimental slope equal to 23000) to be equal to 20 D, for a calculated value equal to 17.3 D (28 D – 10.7 D); actually, for the ICT, these two dipolar moments can be estimated to be collinear.

Table S4 : Computed bond lengths (1-2, 2-3, 3-4, in Å) and Bond Length Alternation (BLA, corresponding to the difference between single and double bond lengths, in Å) for the ground (GS) and first ICT (ES-ICT) and *π-π** (ES-*π-π**) states.



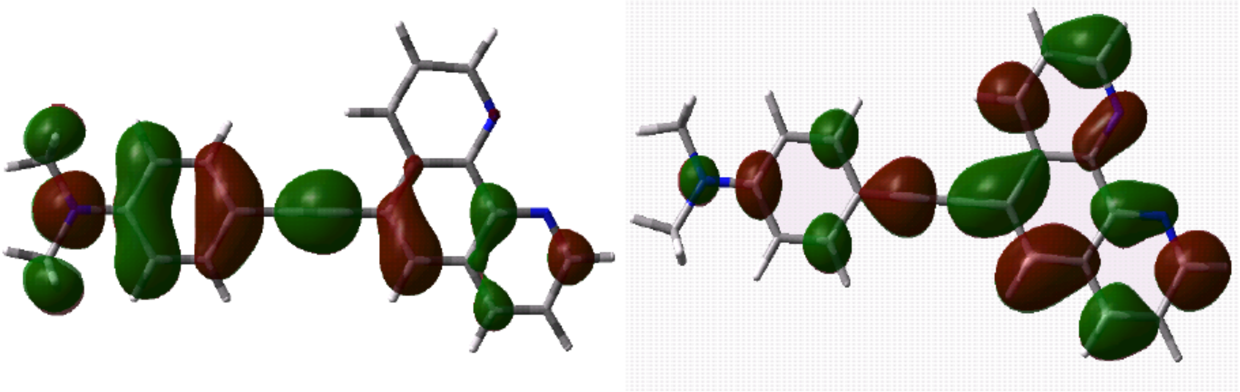
	1-2	**2-3**	**3-4**	**BLA**
GS	1.4148	1.2143	1.4163	0.2012
ES-ICT	1.3880	1.2309	1.3879	0.1571
ES-*π–π**	1.4135	1.2283	1.3887	0.1728

Table S5

Evolution of the vertical lowest energy ICT and *π-π**transitions as a function of *ϕ* torsional angle (rigid scan) computed at PBE0 level.

ϕ (°)	**0**		10		20		30		**40**	
	nm	f	nm	f	nm	f	Nm	f	nm	f
ICT	419	**0.9257**	419	0.9053	419	0.8446	419	0.7444	419	0.6089
*π-π** (LE)	298	0.0530	298	0.0562	300	0.0612	302	0.0528	307	**0.5756**
	50		60		70		80		**90**	
	nm	f	nm	f	nm	f	Nm	f	nm	f
ICT	420	0.4491	420	0.2834	420	0.1372	421	0.0363	415	0.0000
*π-π** (LE)	309	0.4571	312	0.3458	312	0.4314	313	0.5597	312	**0.6103**

Figure S6: The frontier molecular orbitals of **Phen-PENMe$_2$** obtained *via* DFT calculations



HOMO LUMO

Figure S7: 3D schematic representation of the electronic energy levels in Phen-PENMe$_2$ and the related observed transitions; non radiative relaxations are also indicated as grey arrows.