Electronic Supplementary Material (ESI) for Faraday Discussions.

Electronic Supplementary Informations

Solvent tuned single molecule dual emission in protic solvents: effect of polarity and H-bonding

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Computational Details

Density Functional Theory (DFT) and time-dependent DFT Calculations were carried out using the Gaussian 09 suite of programs. All calculations, both at ground and excited state, were carried out using the PBE0 global hybrid functional and a Pople 6-311+G(d,p) double zeta basis set. For all calculations, solvent effects of water were introduced using a conductor-like polarizable continuum model (CPCM) in addition to the explicit, site specific water molecules. Equilibrium orientation of the explicit water molecules was determined by first placing the explicit solvent molecules close to the relevant solvation sites (NMe_2 lone pair and nitrogen atoms located on 1,10-phenanthroline) and conducting a ground state geometry optimisation. All minima on the potential energy surface were verified via the calculation of vibrational frequencies.

All orbitals contours were plotted by means of the Gaussian 09 cubegen utility.

Table S1. Overview of relevant transitions (each indicated by a number) calculated using TD-DFT with the PBE0 exchange-correlation functional and the Pople 6-311+G(d,p) basis set. The orbitals most significant to the transition are given accompanied by their corresponding orbital character. The calculated oscillator strengths; absorption wavelengths and dipole moments are also given.

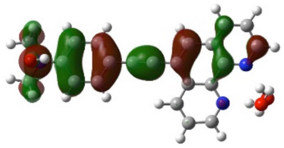
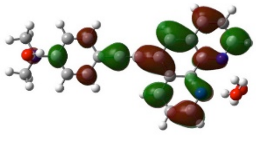
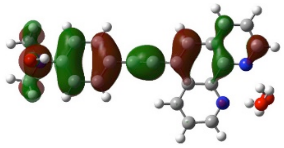
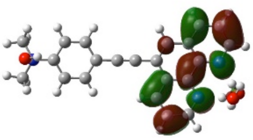
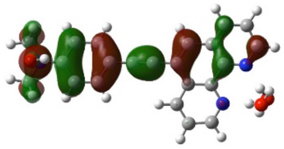
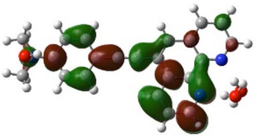
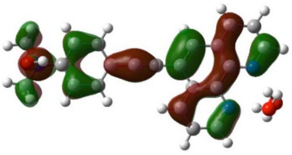
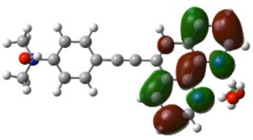
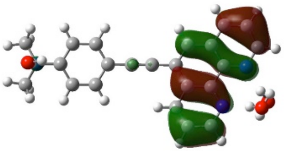
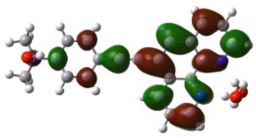
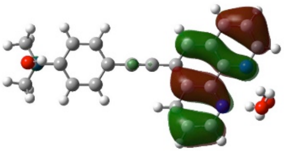
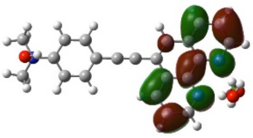
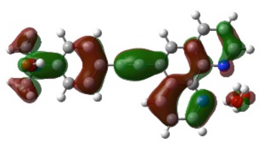
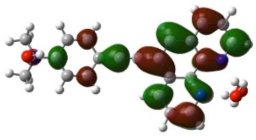
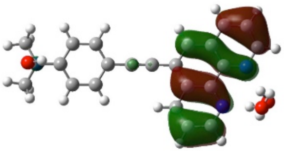
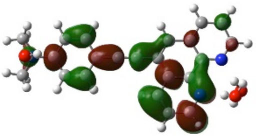
#	*Main Contributing Orbitals*	*Type*	*Starting Orbital*	*Final Orbital*	*f*	*λ (nm)*	*D (Debye)*
1	*HOMO→ LUMO*	$\pi-\pi^*$/ *ICT*			*0.856*	*399*	*17.7*
2	*HOMO→ LUMO+1*	*ICT*			*0.110*	*377*	*24.2*
3	*HOMO→ LUMO+2*	$\pi-\pi^*$/ *ICT*			*0.474*	*302*	*12.2*
5	*HOMO-1→ LUMO+1*	*ICT*			*0.102*	*293*	*11.5*
8	*HOMO-2→ LUMO*	$\pi-\pi^*$			*0.255*	*272*	*3.3*
11	*HOMO-2→ LUMO+1*	$\pi-\pi^*$			*0.583*	*260*	*6.7*
18	*HOMO-6→ LUMO*	*ICT*			*0.103*	*237*	*32.9*
22	*HOMO-2→ LUMO+2*	*ICT*			*0.161*	*226*	*6.4*

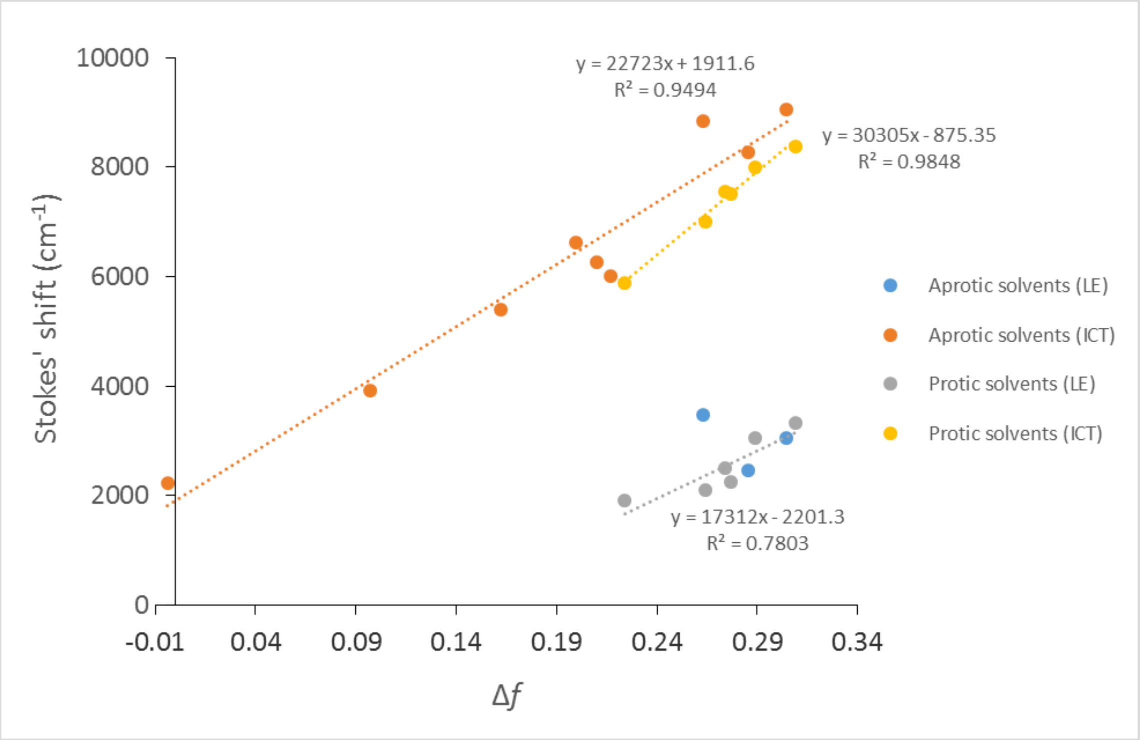
Table S2: Photophysical data of **Phen-PENMe$_2$** in several protic solvents

	Solvents	**1-octanol**	**1-butanol**	**1-propanol**	**2-propanol**	**ethanol**	**methanol**
Absorption	λ_{max} (nm)	382	380	380	378	377	377
	$1/\lambda_{max}$ (cm^{-1})	26178	26316	26316	26455	26525	26525
Emission	λ_{max} (nm)	412	413	420	413	426	431
	$1/\lambda_{max}$ (cm^{-1})	24272	24213	23810	24213	23474	23202
	λ_{max} (nm)	493	518	533	528	540	551
	$1/\lambda_{max}$ (cm^{-1})	20284	19305	18762	18939	18519	18149
Stokes' shift	Stokes' shift LE (cm^{-1})	1906	2103	2506	2242	3051	3323
	Stokes' shift ICT (cm^{-1})	5894	7011	7554	7516	8007	8376
	Δf	0.224	0.264	0.274	0.277	0.289	0.309
	$E_T(30)$	48.1	49.7	50.7	48.4	51.9	55.4

Table S3: Photophysical data of **Phen-PENMe$_2$** in several aprotic solvents

	Solvents	**Cyclohexane**	**Dibutyl-ether**	**Diethyl-ether**	**Ethyl acetate**	**THF**	**Dichloro methane**	**Acetone**	**Acetonitrile**	**DMSO**
Abs	λ_{max} (nm)	371.5	371	369	370	375	379	375	373	383
	$1/\lambda_{max}$ (cm^{-1})	26918	26954	27100	27027	26667	26385	26667	26810	26110
Em	λ_{max} (nm)	x	x	x	x	x	x	413	421	442
	$1/\lambda_{max}$ (cm^{-1})	x	x	x	x	x	x	24213	23753	22624
	λ_{max} (nm)	405	434	461	490	490	491	544	563	579
	$1/\lambda_{max}$ (cm^{-1})	24691	23041	21692	20408	20408	20367	18382	17762	17271
Stokes' shift	Stokes' shift LE (cm^{-1})	x	x	x	x	x	x	2454	3057	3485
	Stokes' shift ICT (cm^{-1})	2227	3913	5408	6619	6259	6019	8284	9048	8839
	Δf	-0.004	0.097	0.162	0.199	0.210	0.217	0.285	0.305	0.263
	$E_T(30)$	30.9	33.0	34.5	38.1	37.4	40.7	42.2	45.6	45.1

Figure S1: Plot of the Stokes' shift against the Lippert-Mataga polarity parameter *Δ*f according to equation (1) for compound **Phen-PENMe$_2$** in several protic and aprotic solvents and for both the LE and the ICT bands.



Lippert-Mataga equation establishes the relationship between the Stokes' shift $\Delta\nu_{\mathrm{ST}}$ 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 $\Delta f(\varepsilon,n)$ 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 S2: Plot of the Stokes's shift against the Dimroth-Reichardt $E_T(30)$ parameter for compound **Phen-PENMe$_2$** in several protic and aprotic solvents and for both the LE and the ICT bands.