SUPPORTING INFORMATION

Dual fluorescence in 9-amino-2,7,12,17-tetraphenylporphycene

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Solvent effects

Several solvents with reported solvatochromic features[1] were chosen to assess the effects of polarity (π^*) and the ability to donate and accept hydrogen bonds (α and β, respectively). No significant absorption and emission shifts were observed, but both steady state fluorescence intensity and decay lifetimes turned out to be highly solvent dependent (Table S1).

Table S1 Steady state fluorescence intensities (F_1 and F_2, λ_{exc} = 647 nm) and fluorescence lifetimes (τ_1 and τ_2, λ_{exc} = 596 nm) measured in different solvents: toluene, tetrahydrofuran (THF), triethylamine (TEA), ethanol, dichloromethane (DCM), chloroform, ethyl acetate (AcOEt), and acetone. The F_1 and F_2 intensities were corrected for the sample absorbance and normalized relative to the largest F_1 intensity.

	F_1	F_2	τ_1 / ns	τ_2 / ns
Toluene	0.822	1.027	0.89	1.79
THF	0.230	0.633	0.43	1.14
TEA	0.382	0.152	0.58	1.24
Ethanol	0.304	0.577	0.50	1.08
DCM	0.790	0.770	0.71	1.44
Chloroform	1.000	0.906	0.80	1.53
AcOEt	0.309	0.702	0.51	1.48
Acetone	0.269	0.567	0.43	1.17

Table S2 shows the dependence of the normalized fluorescence intensity and the fluorescence lifetimes (τ_1 and τ_2) on the solvent parameters α, β and π^*. While the F_2 intensity does not significantly correlate with none of the linear combinations of these parameters, the intensity of F_1 shows a remarkable dependence on β and π^*. Similarly, τ_1 becomes faster when π^* and β are increased, but no significant correlation could be observed for the τ_2 values.

Table S2 Multiple regression of normalized intensities (F_1 and F_2) and fluorescence lifetimes (τ_1 and τ_2) depending on the α, β and π^* parameters of the solvent shown in Table 1. Data were fitted to the equation $Y = A\alpha + B\beta + P\pi^* + C$, where *Y* is either the steady state normalized intensity or the fluorescence lifetime in ns. *P*-value and R^2 are also shown.

	A	B	P	C	*P*-value	R^2
F_1	0.343	–1.153	–0.765	1.309	< 0.001	0.988
F_2	0.076	–0.555	0.345	0.672	0.168	0.683
τ_1 / ns	0.143	–0.645	–0.563	1.139	0.026	0.879
τ_2 / ns	–0.110	–0.772	–0.481	1.946	0.100	0.759

Computational calculations

Table S3 TD-DFT 6-31G(d) calculations for all possible tautomers of 9-ATPPo. *E* is the energy in eV and *f* is the oscillator strength of the corresponding transition from S_0. The ground state energy of ***trans*-1** has been used as reference.

Tautomer	**State**	***E*/eV**	***f***	**Main Configuration**
***trans*-1**	S_0	0		
	S_1	1.852	0.3088	68.85%(0-0), 10.39(1-1), 2.84%(1-0)
	S_2	2.241	0.3313	65.84%(1-0), 19.64(0-1)
***trans*-2**	S_0	0.009		
	S_1	1.982	0.4383	67.01%(0-0), 10.82%(1-1)
	S_2	2.155	0.1714	71.13%(1-0), 19.15%(0-1)
***cis*-A1**	S_0	0.074		
	S_1	2.084	0.3790	63.05%(0-0), 10.09%(1-1), 8.72%(1-0)
	S_2	2.249	0.2517	63.72%(1-0), 16.05%(0-1), 5.92%(0-0)
***cis*-A2**	S_0	0.097		
	S_1	1.931	0.2935	66.76%(0-0), 8,86%(1-1), 4.43%(1-0)
	S_2	2.286	0.2861	63.65%(1-0), 20.33%(0-1), 3.08%(0-0)
***cis*-B1**	S_0	1.340		
	S_1	3.221	0.3129	69.19%(0-0), 10.14%(1-1), 2.24%(2-0)
	S_2	3.490	0.1368	66.26%(1-0), 13.64%(0-1), 6.39%(2-0)
***cis*-B2**	S_0	1.236		
	S_1	3.104	0.2515	70.45%(0-0), 10.38%(1-1), 2.17%(2-0)
	S_2	3.416	0.126	68.64%(1-0), 19.16%(0-1), 2.94%(3-0)

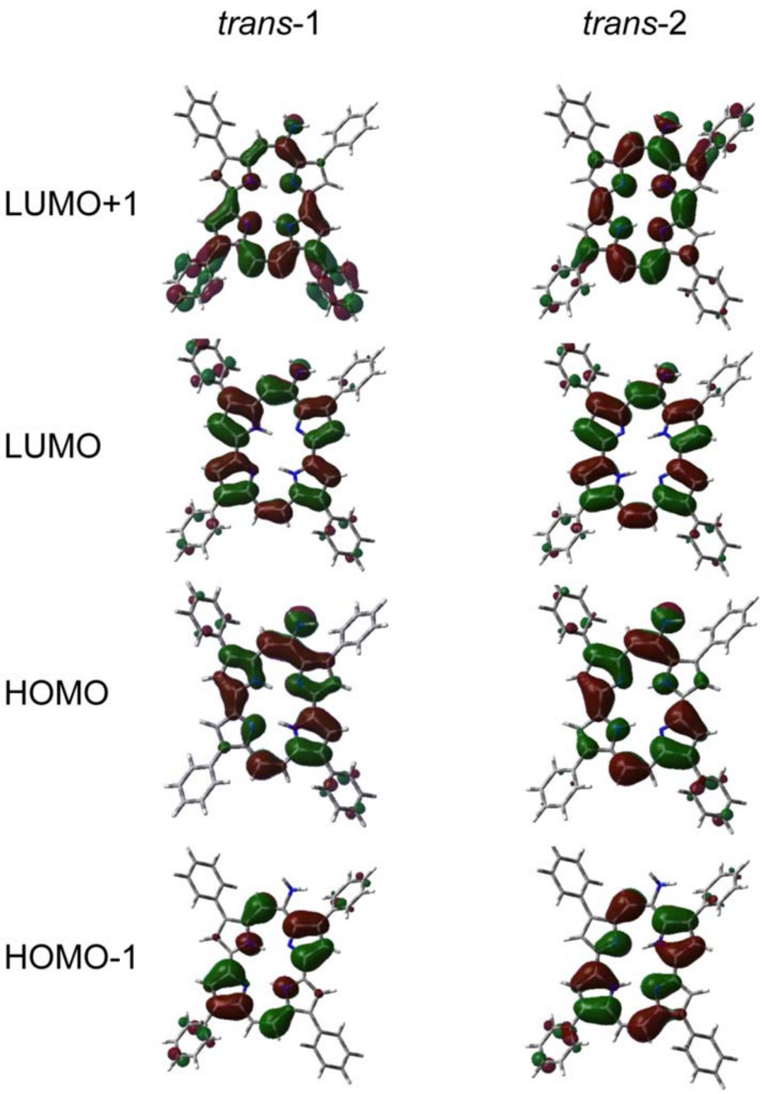

Fig. S1 Orbital topologies of ***trans*-1** and ***trans*-2**.

References

1. M. J. Kamlet, J.L.M. Abboud, M.H. Abraham and R.W. Taft, *J. Org. Chem.*,1983, **48**, 2877–2887.