A TDDFT/MMPol/PCM model for the simulation of Exciton-Coupled Circular Dichroism spectra

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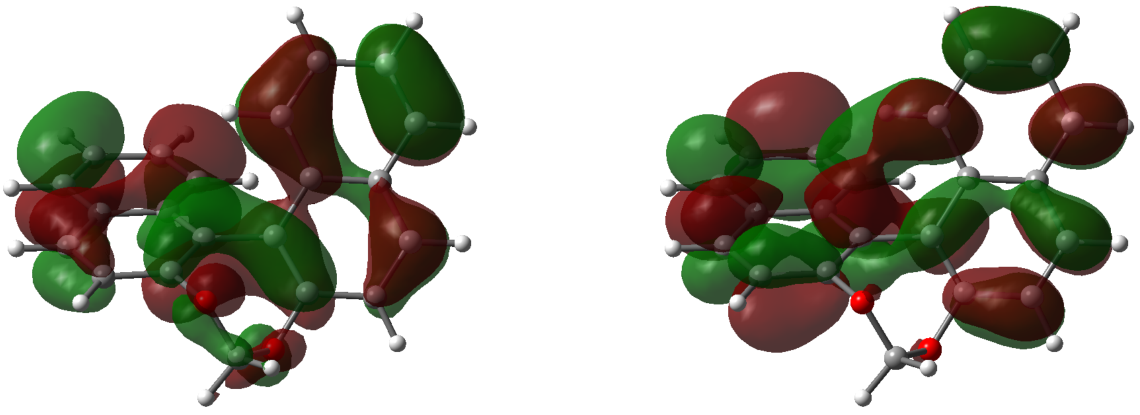
Supporting Information

Figures



HOMO LUMO+1

Figure S1. Molecular Orbitals of DCD computed in vacuo at cam-B3LYP/6-31+G(d) level of theory involved in the transition at 260 nm resulting in a weak positive band close to the strong ^1B_b couplet in the simulated CD spectrum.

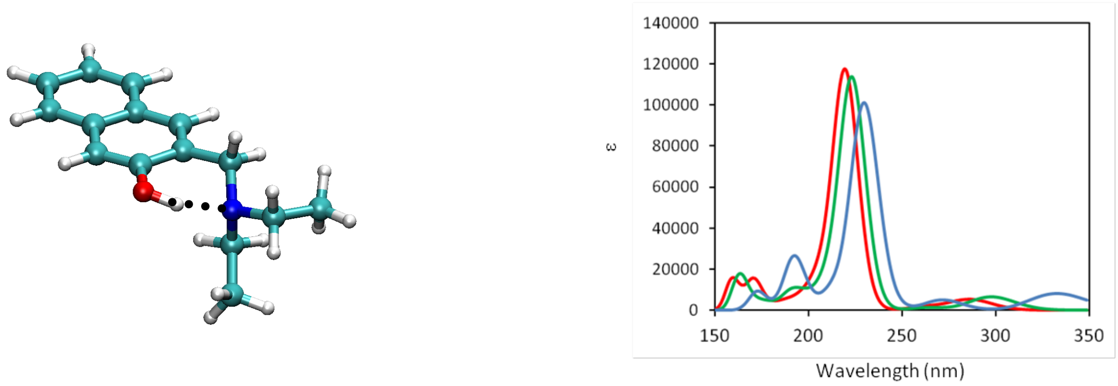


Figure S2. deaNpO TD cam-B3LYP/6-31+g(d)/PCM absorption spectra (right) computed on the optimized structures obtained by a relaxing scan of the N-H bond coordinate at m062x/6-311+g(d,p) level of theory in vacuo (left). We sampled three different N-H distances: 1.70 Å (red line), 1.30 Å (green line) and 0.90 Å (blue line). The ^1B_b peak shifted to longer wavelength passing from the neutral form to the zwitterionic form of BINOLAM monomer and a peak near 200 nm, related to the high energy ^1B_a transition appeared.

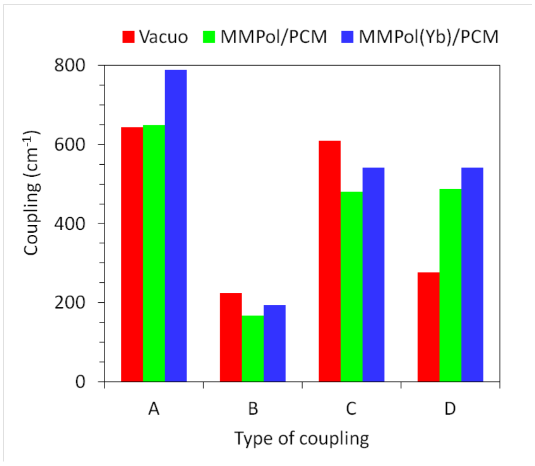


Figure S3. Coupling terms (cm^{-1}) between the ^1B_b transition of the chromophore pairs computed at cam-B3LYP/6-31g(d) level of theory with different environmental treatments. We report the average values calculated by regrouping the symmetrical equivalent couplings as follow: group A (intra) = V_{12}, V_{34}, V_{56}; group B = V_{16}, V_{23}, V_{45} ; group C = V_{13}, V_{15}, V_{24},V_{26}, V_{35}, V_{46} ; group D = V_{14}, V_{25}, V_{36}. The average distances of the chromophore centers for the four groups are 4.71, 6.76, 7.99 and 9.71 Å respectively. The labels are referred to the Figure 10.

Tables

		E(eV)	**E** (nm)	μ^2 (D^2)	ϑ (deg)
SAC-CI 6311+G(d,p)	^1L_b	3.729	332.5	4.7	**-30**
	^1L_a	3.965	312.4	8.3	**29**
	^1B_b	5.239	236.7	32.5	**29**
	^1B_a	-	-	-	**-**
cam-B3LYP 6-31G(d)	^1L_b	3.309	374.7	6.4	**-39**
	^1L_a	4.448	278.8	5.4	**18**
	^1B_b	5.648	219.5	36.7	**18**
	^1B_a	6.794	182.5	12.9	**-39**
cam-B3LYP 6-31+G(d)	^1L_b	3.274	378.7	6.8	**-37**
	^1L_a	4.140	299.5	5.2	**23**
	^1B_b	5.427	228.4	20.3	**10**
	^1B_a	6.560	189.0	12.5	**-48**
cam-B3LYP 6-311+G(d)	^1L_b	3.263	380.0	6.5	**-37**
	^1L_a	4.143	299.2	5.3	**23**
	^1B_b	5.413	229.0	18.0	**10**
	^1B_a	6.548	189.4	12.0	**-48**

Table S1. TD bright states of NpO$^-$ computed at different level of theory in vacuo. The rotation angle of the transition dipole moments is referred to the long axis of naphthalene.

		E(eV)	**E** (nm)	μ^2 (D^2)	ϑ (deg)
SAC-CI 6-311+G(d)	^1L_a	2.734	454	7.2	**-57**
	^1L_b	3.978	312	5.8	**6**
	^1B_b	5.286	235	44.2	**11.5**
	^1B_a	-	-	-	**-**
cam-B3LYP 6-31G(d)	^1L_a	3.496	354.6	5.6	**-53**
	^1L_b	4.596	269.8	2.4	**5**
	^1B_b	5.644	219.7	47.4	**10**
	^1B_a	6.551	189.3	9.3	**-40**
cam-B3LYP 6-31+G(d)	^1L_a	3.510	353.3	5.8	**-52**
	^1L_b	4.430	279.9	2.2	**8**
	^1B_b	5.445	227.7	40.7	**8**
	^1B_a	6.362	194.9	7.5	**-38**
cam-B3LYP 6-311+G(d)	^1L_a	3.494	354.8	5.6	**-52**
	^1L_b	4.438	279.4	2.7	**6**
	^1B_b	5.438	228.0	47.1	**9**
	^1B_a	6.343	195.5	9.4	**-36**

Table S2. TD bright states of deaNpO computed at different level of theory in vacuo. The rotation angle of the transition dipole moments is referred to the long axis of naphthalene.