

Supporting Information

Combined effect of hydrogen bonding interactions and freezing of rotameric equilibrium on the enhancement of photostability

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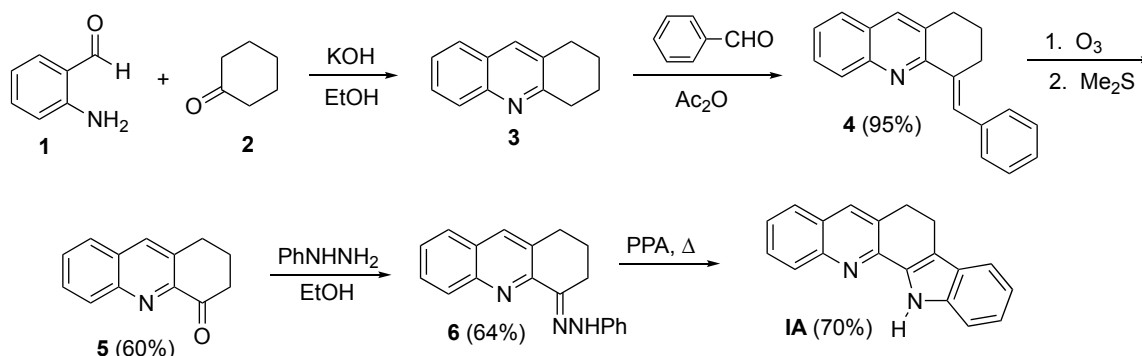
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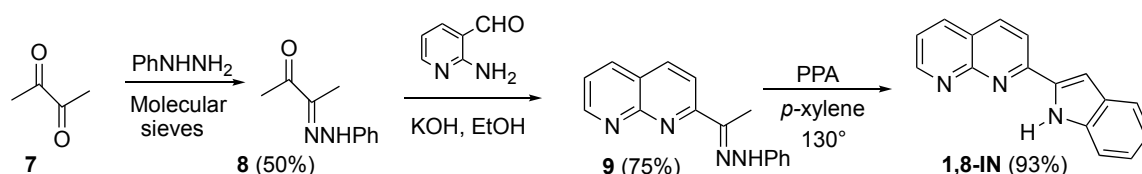
Preparation of 12,13-Dihydro-5H-indolo[3,2-c]acridine (IA)

The Friedländer condensation of 2-aminobenzaldehyde with cyclohexanone provides the tetrahydroacridine **3**. Subsequent condensation with benzaldehyde in the presence of acetic anhydride gives the benzylidene derivative **4**.^[37] Ozonolysis of **4** followed by a reductive workup gives the ketone **5** which then affords the hydrazone **6** after reaction with phenylhydrazine in EtOH. Fisher indolization of **6** provides the indole derivative **IA**.^[38]



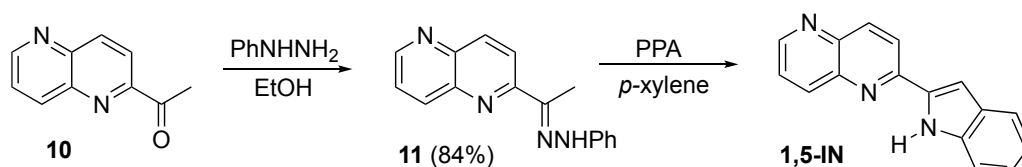
Preparation of 2-(1'*H*-indol-2'-yl)-[1,5]naphthyridine (1,8-IN)

The treatment of 2,3-butanedione (**7**) with phenylhydrazine in the presence of molecular sieves provided the monophenylhydrazone derivative **8**. Subsequent Friedländer condensation of **8** with 2-aminonicotinaldehyde gave the 1,8-naphthyridine derivative **9** which underwent reaction with polyphosphoric acid to afford **1,8-IN**.^[36]



Preparation of 2-(1'*H*-indol-2'-yl)-[1,8]naphthyridine (1,5-IN)

The reaction of 2-acetyl-1,5-naphthyridine (**10**) with phenylhydrazine gave the phenylhydrazone derivative **11**. Heating **11** with polyphosphoric acid in *p*-xylene afforded **1,5-IN**.^[36]



References

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- 37 Y. Jahng, R. P. Thummel and S. G. Bott, *Inorg. Chem.*, 1997, **36**, 3133–3138.
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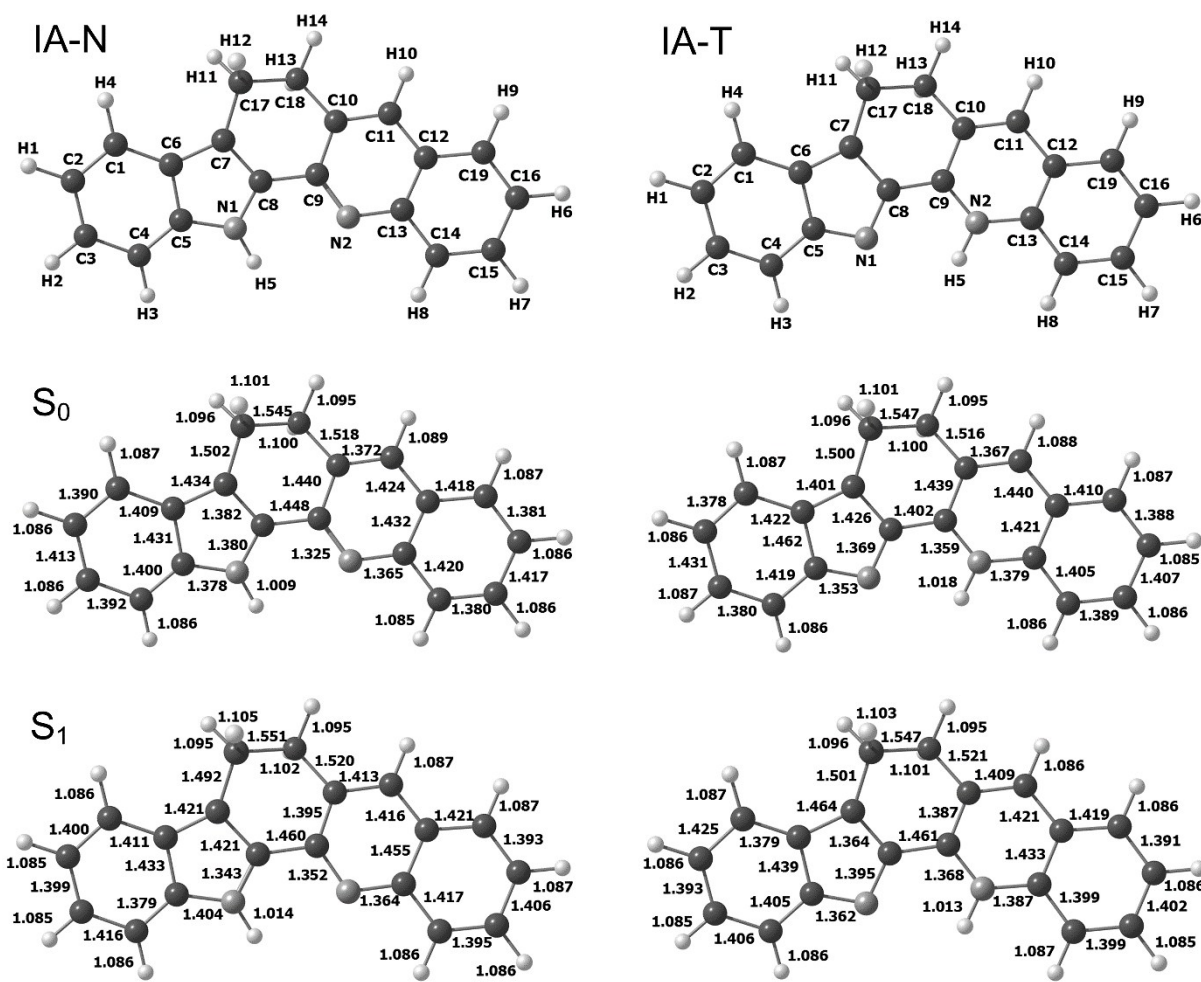


Figure S1. DFT/B3LYP/6-31G+(d,p) optimized structures of **IA-N** and **IA-T** in the ground (S_0) and in the first excited singlet (S_1) states. The bond lengths (Å) are also given for comparison.

Table S1. Selected DFT calculated torsion angles ($^\circ$) of **IA-N** and **IA-T**. Labeling refers to Figure S1.

Parameter	IA-N		IA-T	
	S_0	S_1	S_0	S_1
φ C8-C7-C19-C18	27.7	31.4	35.4	29.1
φ C9-C10-C18-C19	36.1	32.6	27.7	33.8
φ C7-C19-C18-C10	-43.8	-44.4	-43.1	-43.7
φ C7-C8-C9-C10	-10.8	-10.1	-9.1	-11.3
φ C9-C8-C7-C19	-0.4	-4.7	-8.5	-2.0
φ C8-C9-C10-C18	-8.1	-5.0	-1.8	-5.8
φ N1-C8-C9-N2	-7.9	-9.5	-5.6	-9.5

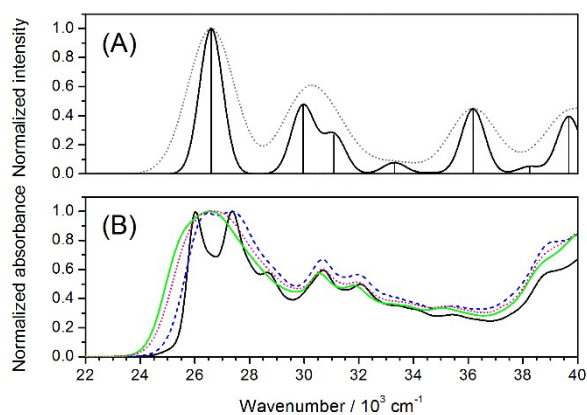


Figure S2. (A) Normalized UV-Vis absorption spectra of **1A** computed at the TDDFT/B3LYP/6-31+G(d,p) level for the DFT/B3LYP/6-31+G(d,p) optimized ground-state geometry. The spectral envelopes were obtained by convolution of the respective stick spectra with a Gaussian function of 2000 cm^{-1} fwhm (grey dotted line) and 1000 cm^{-1} fwhm (black solid line). (B) Normalized experimental absorption spectra recorded for **1A** dissolved in *n*-hexane (black solid line), acetonitrile (blue dashed line), 1-propanol (green solid line), and methanol (pink dotted line).

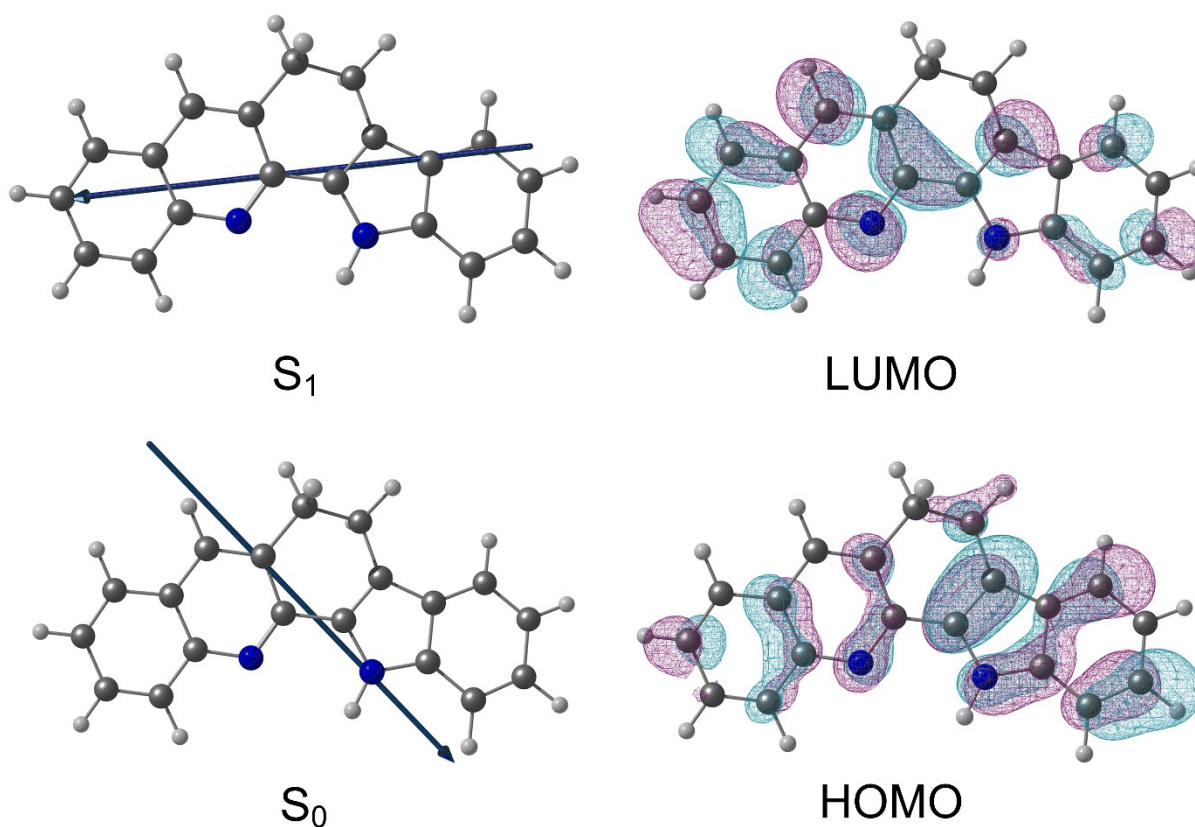


Figure S3. B3LYP and TD-B3LYP/6-31+G(d,p) calculated S_0 and S_1 dipole moments and shapes of molecular orbitals engaged in $S_1 \leftarrow S_0$ transition (represented by LUMO $\leftarrow$ HOMO in more than 90%).

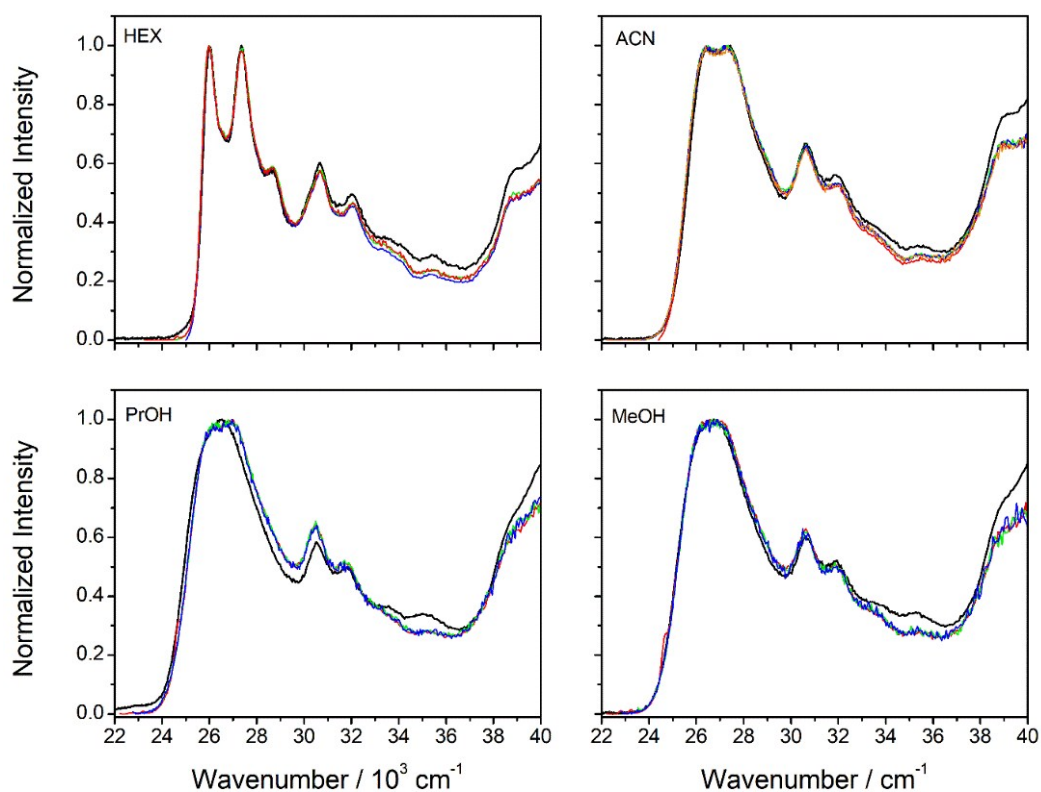


Figure S4. Comparison of normalized fluorescence excitation spectra with absorption spectra of IA in n-hexane (HEX), acetonitrile (ACN), 1-propanol (PrOH), and methanol (MeOH). Black line represents the absorption, the red, green, and blue lines belong to the bands of fluorescence excitation spectra determined with different emission energies.

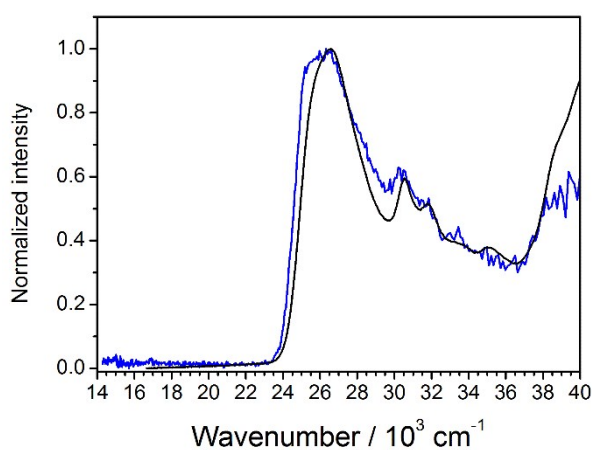


Figure S5. The comparison of normalized fluorescence excitation spectra (blue line) with absorption spectra (black line) of **IA** in 1-propanol determined for tautomeric emission band at 13500 cm⁻¹.

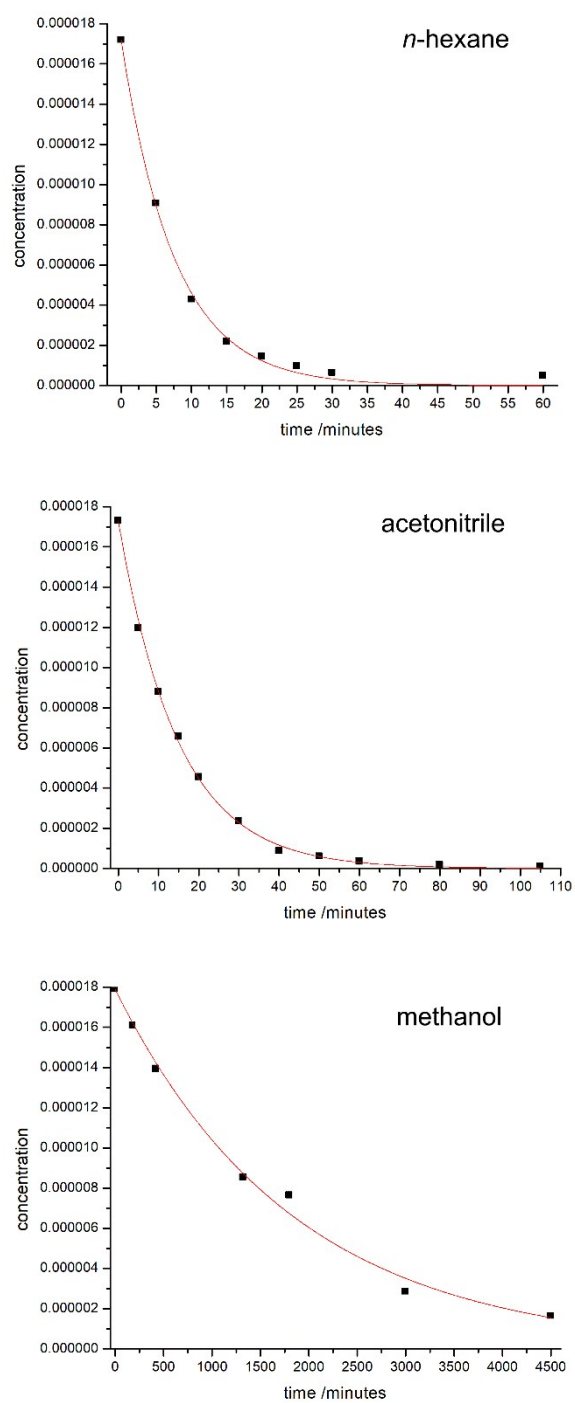


Figure S6. LCMS kinetic profiles of **IA** photodegradation.