SUPPORTING INFORMATION

Azapyrene-based fluorophores: synthesis and photophysical properties

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Density functional theory (DFT)

The calculation was carried out in the Orca 4.0.1 software package [1] using the DFT B3LYP, 6-311G* method [2]. Calculations in DCM were performed using CPCMC solvation model in Orca package. TD-DFT calculations were performed for up to 20 excited states in the energy window from -3 to 3. Visualization of TD-DFT UV-Vis spectra was carried out in the ChemCraft program, the Gaussian band broadening method, the half-width of the band was assumed to be 7. The energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), energy gaps and dipole moments were calculated for the DFT-optimized structures of pyrene **1** and azapyrene **2-5** (Figure S1). Our work was performed using "Uran" supercomputer of IMM UB RAS.

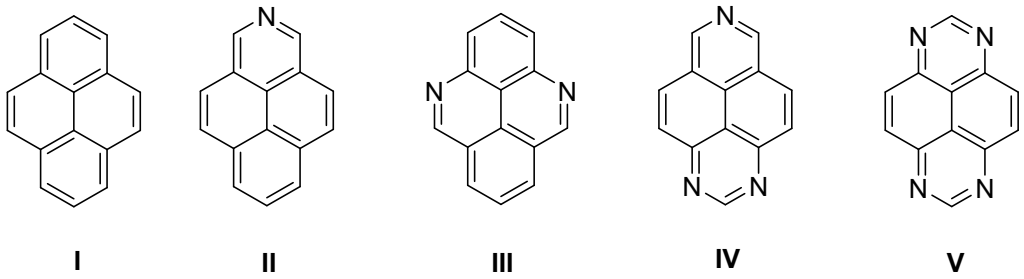
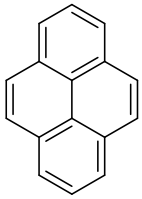
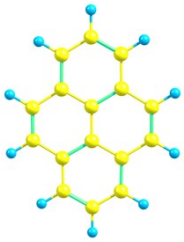
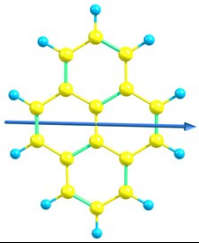
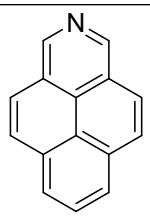
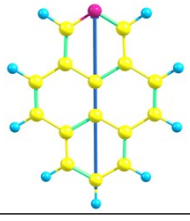
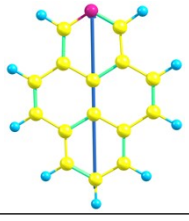


Figure S1 Chemical structures of pyrene (I), 2-azapyrene (II), 4,10-diazapyrene (III), 1,3,7-triazapyrene (IV), 1,3,6,8-tetraazapyrene (V)

Table S1 Calculated energy of HOMO/LUMO, energy gaps and dipole moments of pyrene **I** and azapyrenes II-**V** based on B3LYP/6-311G* functional (gas phase)

#	HOMO, eV	LUMO, eV	ΔE, eV	μ (DCM), D
I	-5.4805	-1.6360	3.8445	0.00197
II	-5.7289	-1.8709	3.8580	3.08637
III	-6.1393	-2.2473	3.8920	3.89782
IV	-6.6053	-2.6118	3.9935	1.33724
V	-7.1585	-3.1004	4.0581	0.00021

Table S2 Calculated dipole moments of pyrene I and azapyrenes II-**V** based on B3LYP/6-311G* functional

#	Structure	μ, D (gas phase)	μ, D (in DCM)
I		0.00000 	0.00197 
II		2.76286 	3.08637 

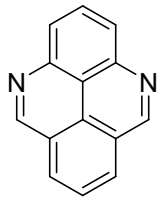
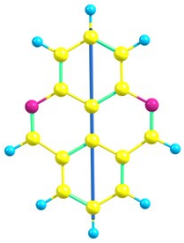
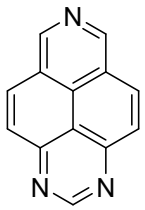
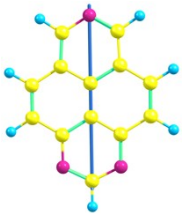
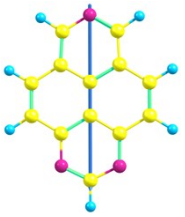
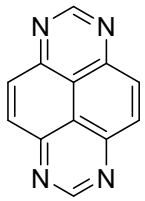
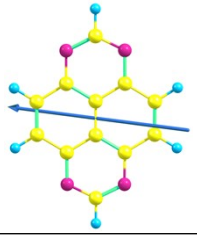
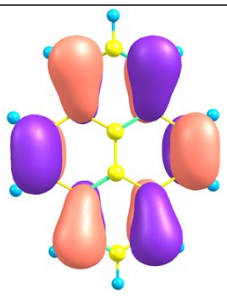
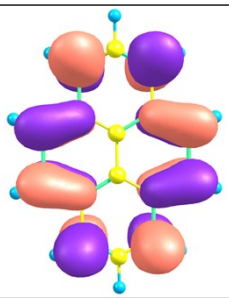
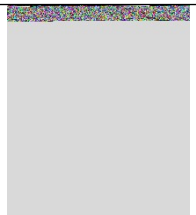
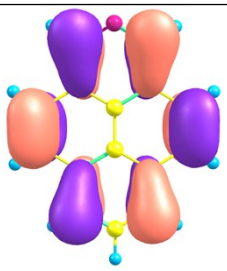
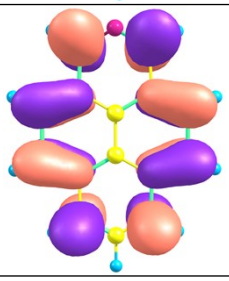
III		2.49885 	3.89782 
IV		1.19399 	1.33724 
V		0.00000 	0.00021 

Table S3 Imaging of HOMO/LUMO of pyrene 1 and azapyrenes 2-5 based on B3LYP/6-311G* functional

#	Compound	HOMO	LUMO
I			
II			

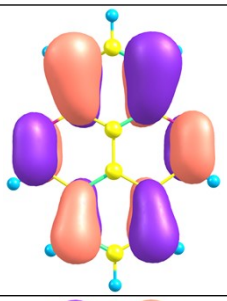
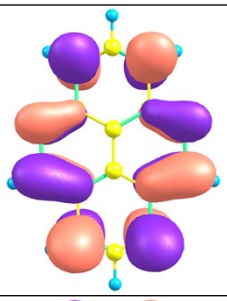
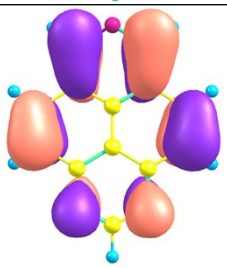
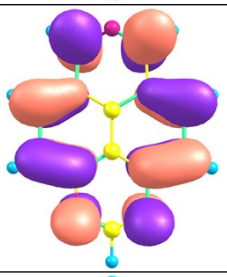
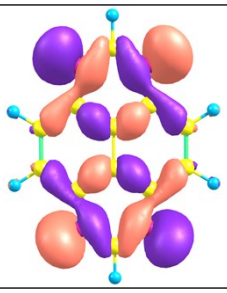
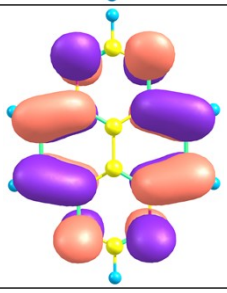
III			
IV			
V			

Table S4 Data of Maximum of Calculated Spectrum of Absorbance (**1-5**)

#	Maximum of Calculated Spectrum of Absorbance, nm
I	167, 183, 217, 255, 318
II	173, 183, 216, 252, 262, 317, 328
III	168, 186, 213, 243, 324
IV	172, 181, 212, 245, 255, 310, 336
V	176, 185, 214, 237, 295, 318, 394

TD-DFT calculations of the UV-Vis spectra

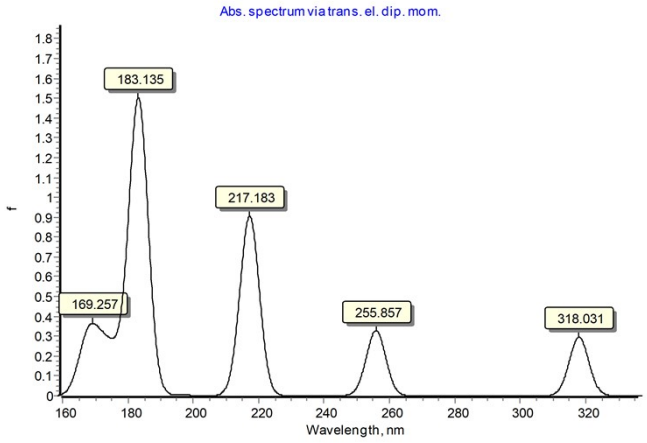


Fig. S2 DFT UV-vis of pyrene I

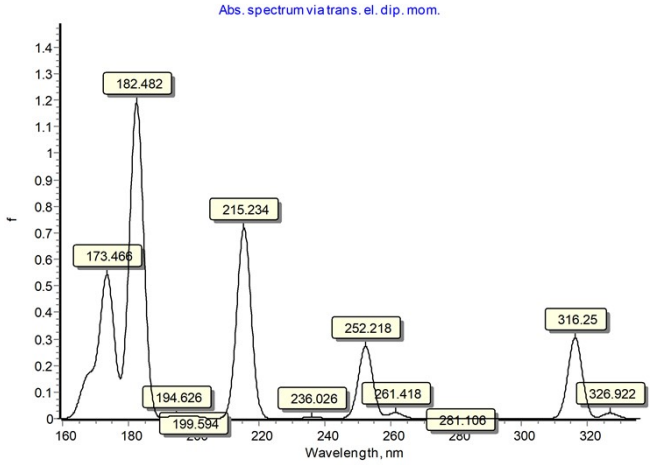


Fig. S3 DFT UV-vis of 2-azapyrene II

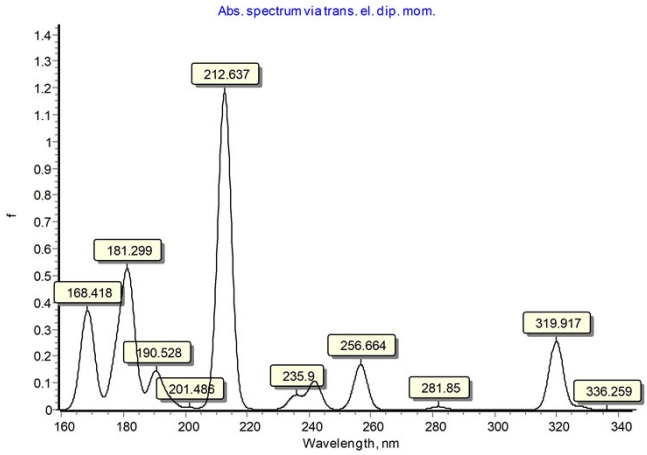


Fig. S4 DFT UV-vis of 4,10-diazapyrene III

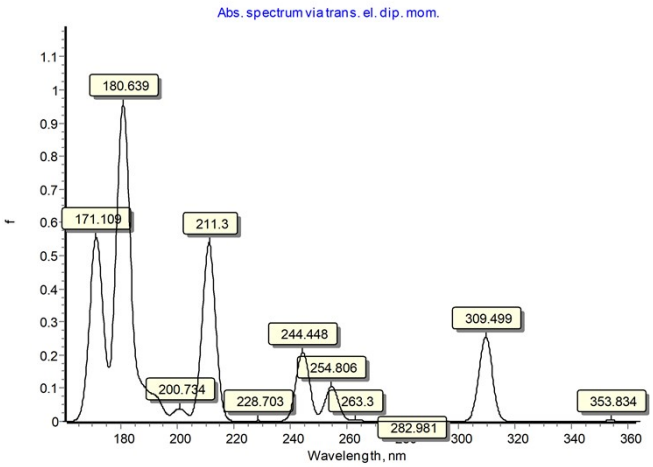


Fig. S5 DFT UV-vis of 1,3,7-triazapyrene IV

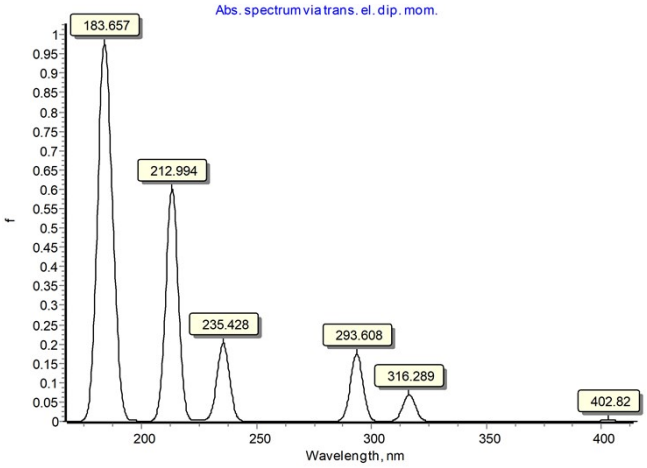


Fig. S6 DFT UV-vis of 1,3,6,8-tetraazapyrene V

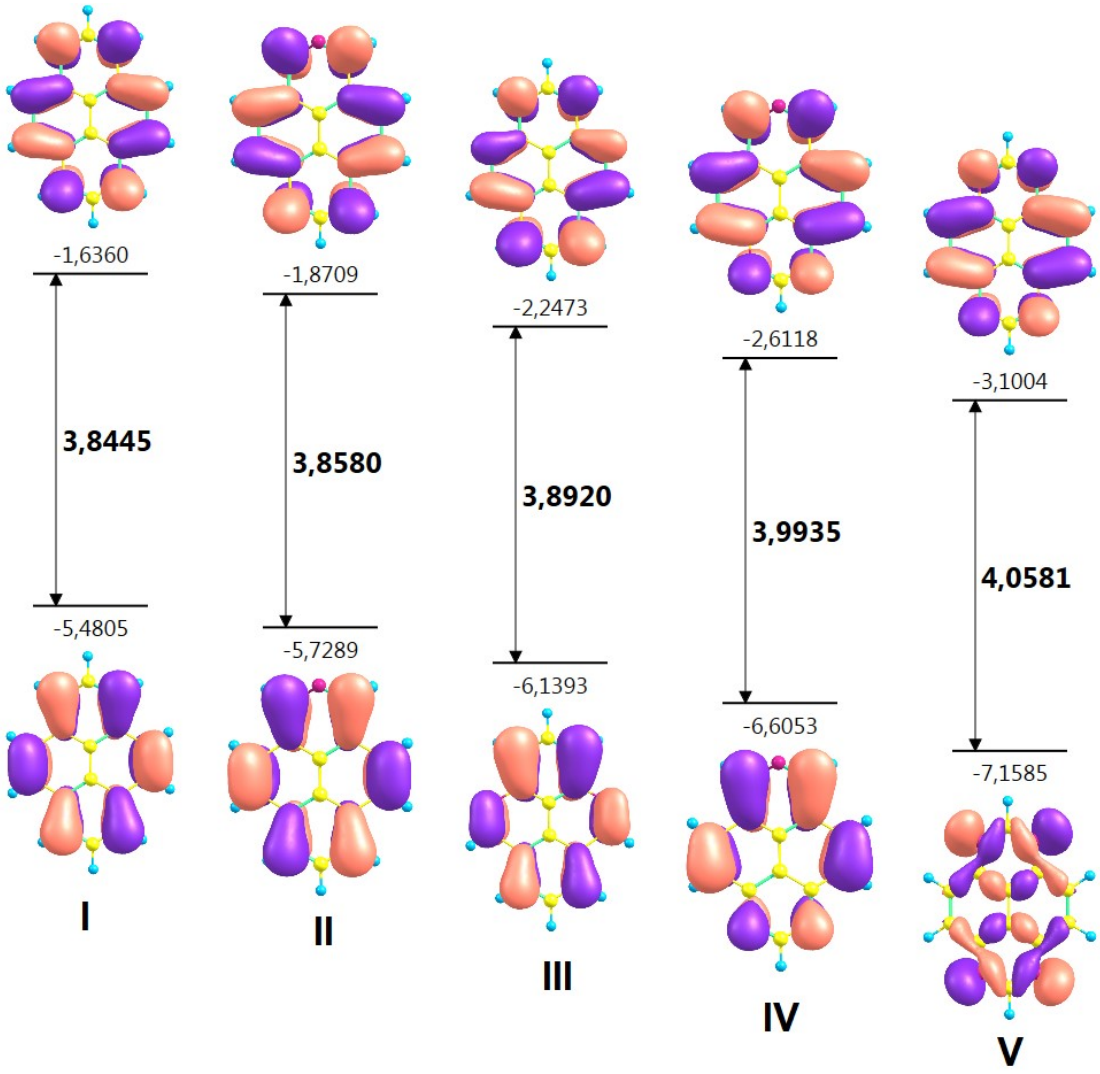


Fig. S7 Calculated energy of HOMO/LUMO and energy gaps of pyrene I and azapyrenes II-V based on B3LYP/6-311G* functional (gas phase)

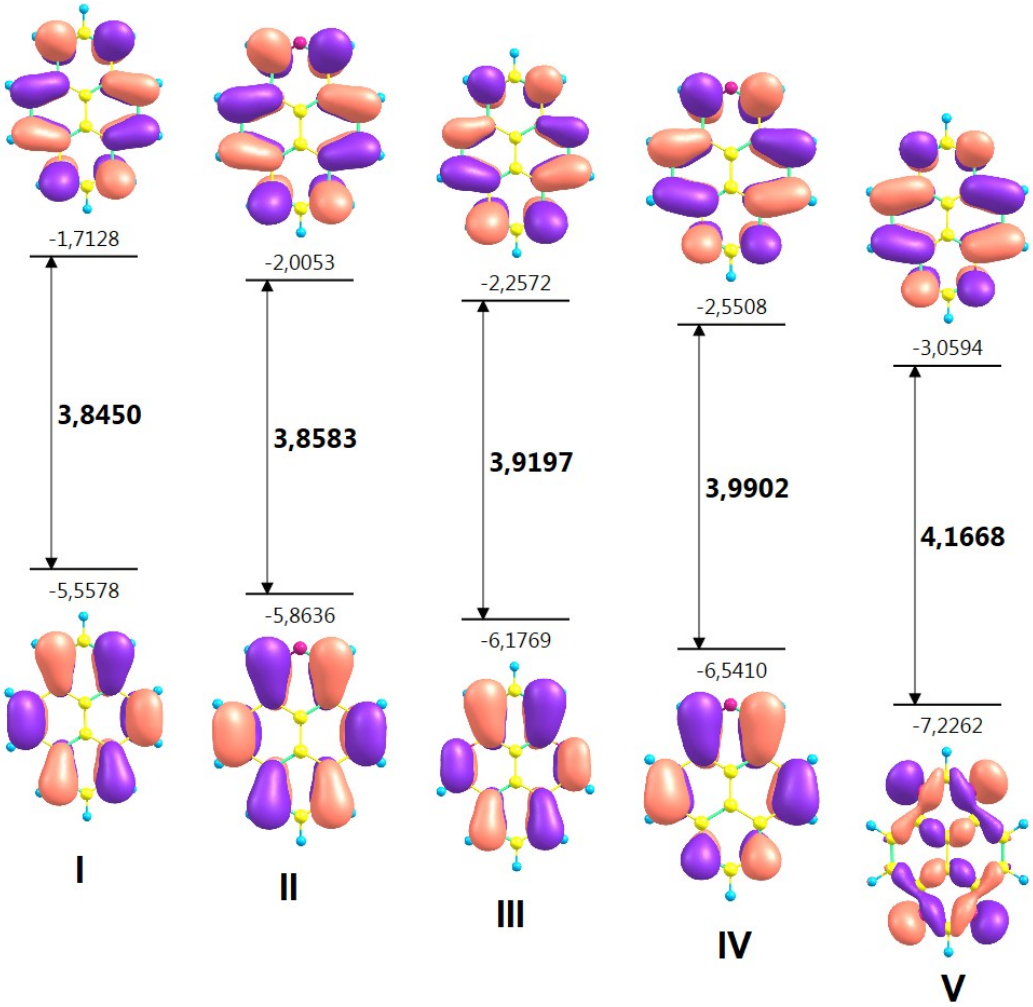


Fig. S8 Calculated energy of HOMO/LUMO and energy gaps of pyrene I and azapyrenes II-V based on B3LYP/6-311G* functional (CH_2Cl_2 phase)

References

1 F. Neese, The ORCA program system, Wiley interdisciplinary Reviews - Computational Molecular Science, 2012, 2, 73.

2 (a) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions, J. Chem. Phys., 1980, 72, 650;(b) A. D. McLean and G. S. Chandler, Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, Z=11–18, J. Chem. Phys.,1980, 72, 5639; (c) T. Clark, J. Chandrasekhar and P. v. R. Schleyer, Efficient diffuse function-augmented basis sets for anion calculations. III. The 3-21+G basis set for first-row elements, Li–F, J. Comp. Chem.,1983, 4, 294; (d) M. J. Frisch, J. A. Pople and J. S. Binkley, Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets, J. Chem. Phys., 1984, 80, 3265.