Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Mixed *N*-Aryl/Alkyl Substitution Favours an Unusual Tautomer of Near-Infrared Absorbing Azacalixphyrins

Lucien Lavaud,[a] Cloé Azarias,[b] Gabriel Canard,[a] Simon Pascal,*[a] Denis Jacquemin*[b] and Olivier Siri*[a]

[a] *Aix Marseille Univ, CNRS UMR 7325, CINAM, Campus de Luminy, case 913, 13288 Marseille cedex 09, France. E-mail: pascal@cinam.univ-mrs.fr; olivier.siri@univ-amu.fr*

[b] *Université de Nantes, CNRS, CEISAM UMR 6230, F-44000 Nantes, France. E-mail: Denis.Jacquemin@univ-nantes.fr*

[c] Present address : LaboLife France, 1, rue François Bruneau, 44000 Nantes, France.

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S-I. ^{1}H AND ^{13}C NMR SPECTRA

Compound 4a

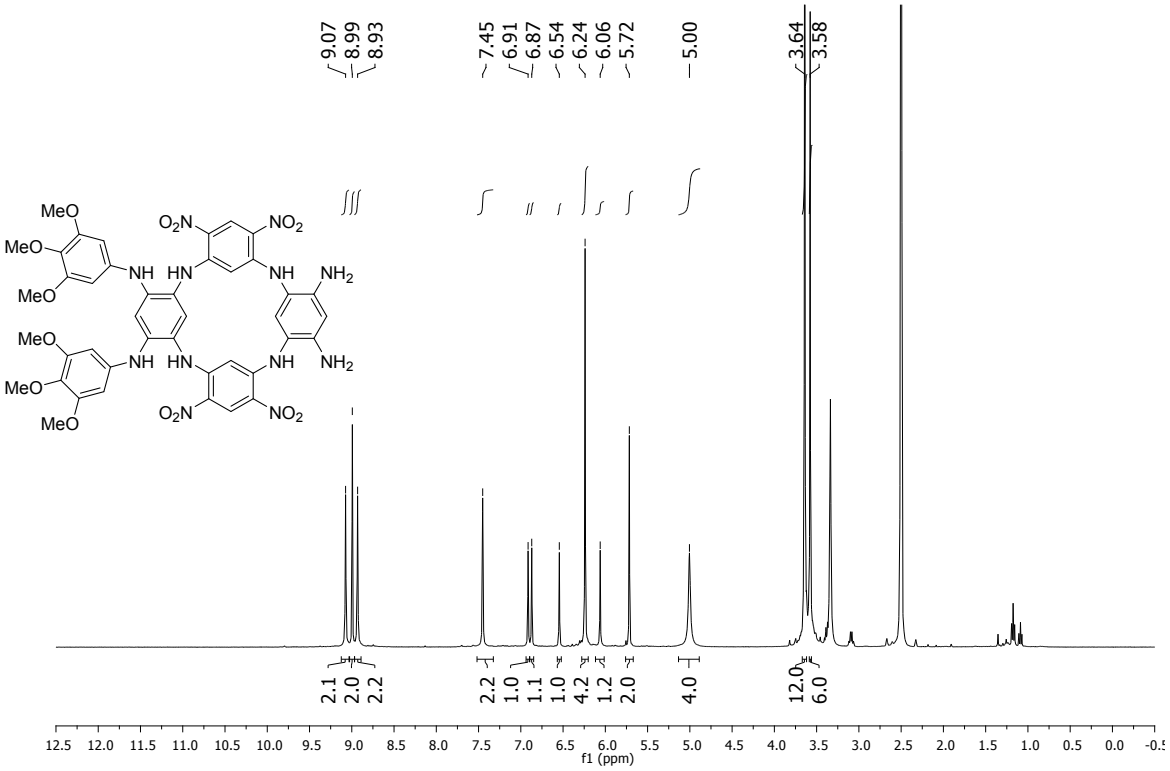


Figure S 1. ^{1}H NMR (400 MHz, DMSO) for compound **4a**.

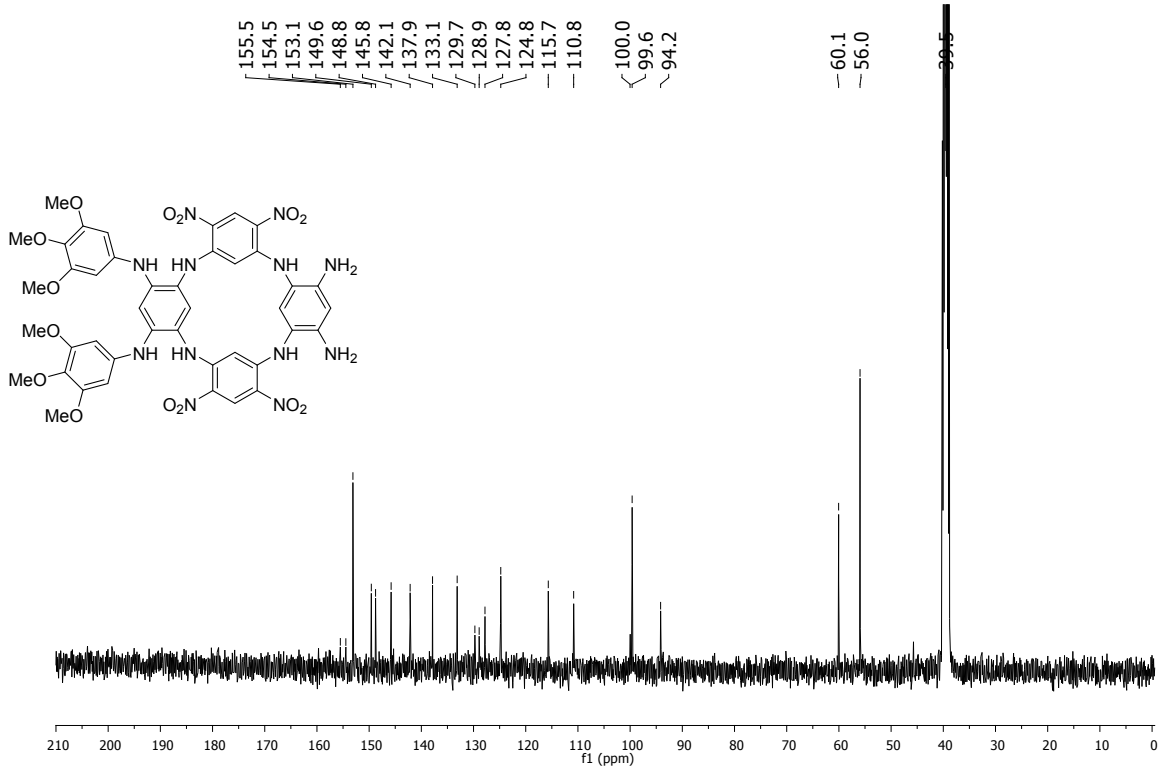


Figure S 2. ^{13}C NMR (101 MHz, DMSO) for compound **4a**.

Compound 4ab

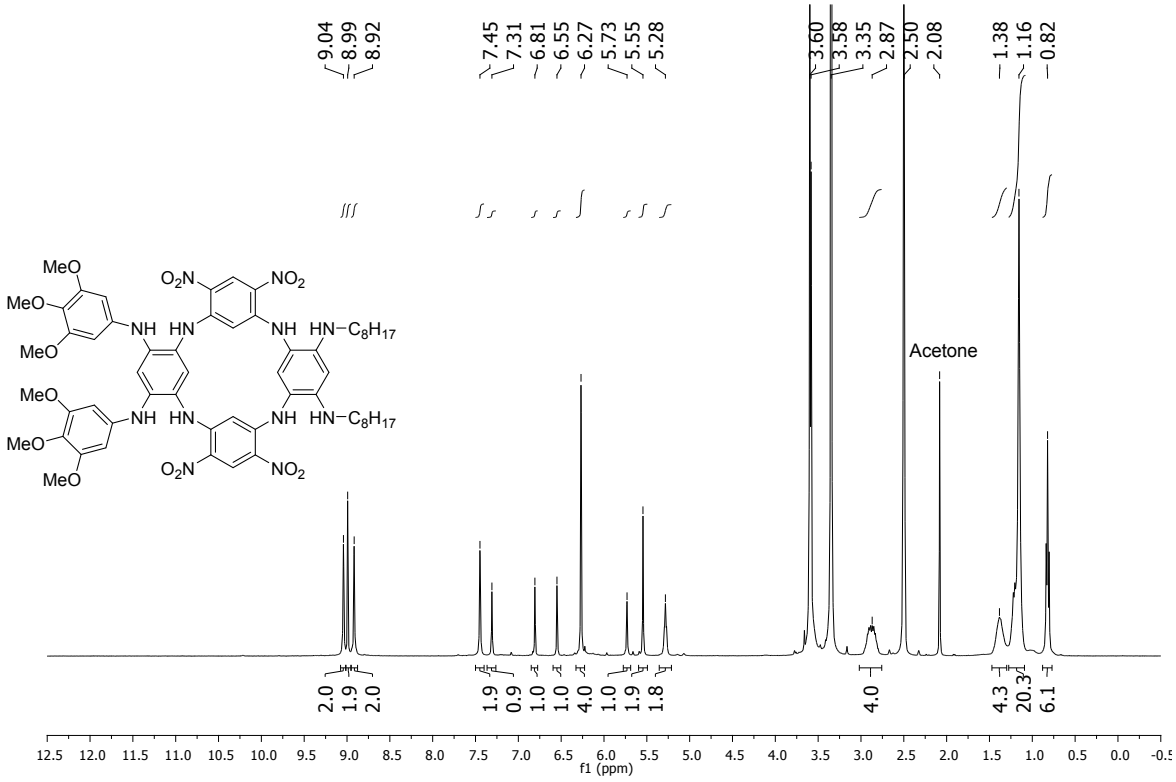


Figure S 3. ^{1}H NMR (400 MHz, DMSO) for compound **4ab**.

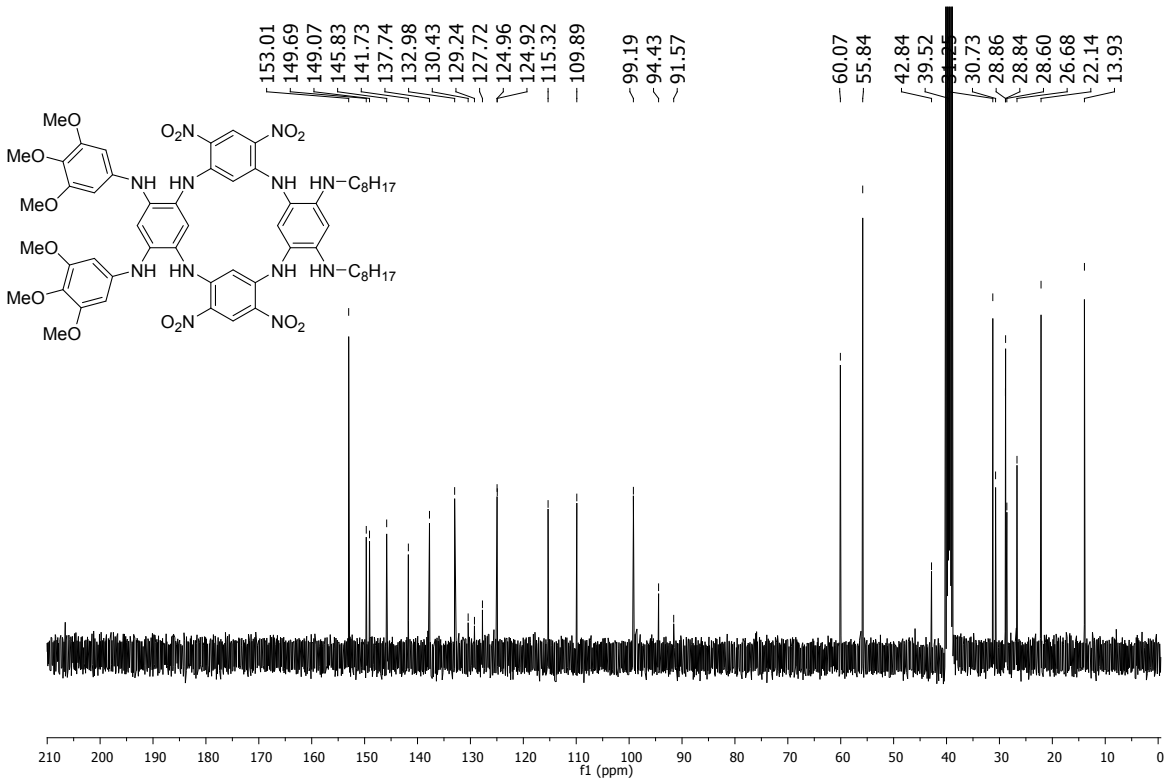


Figure S 4. ^{13}C NMR (101 MHz, DMSO) for compound **4ab**.

Compound 1a

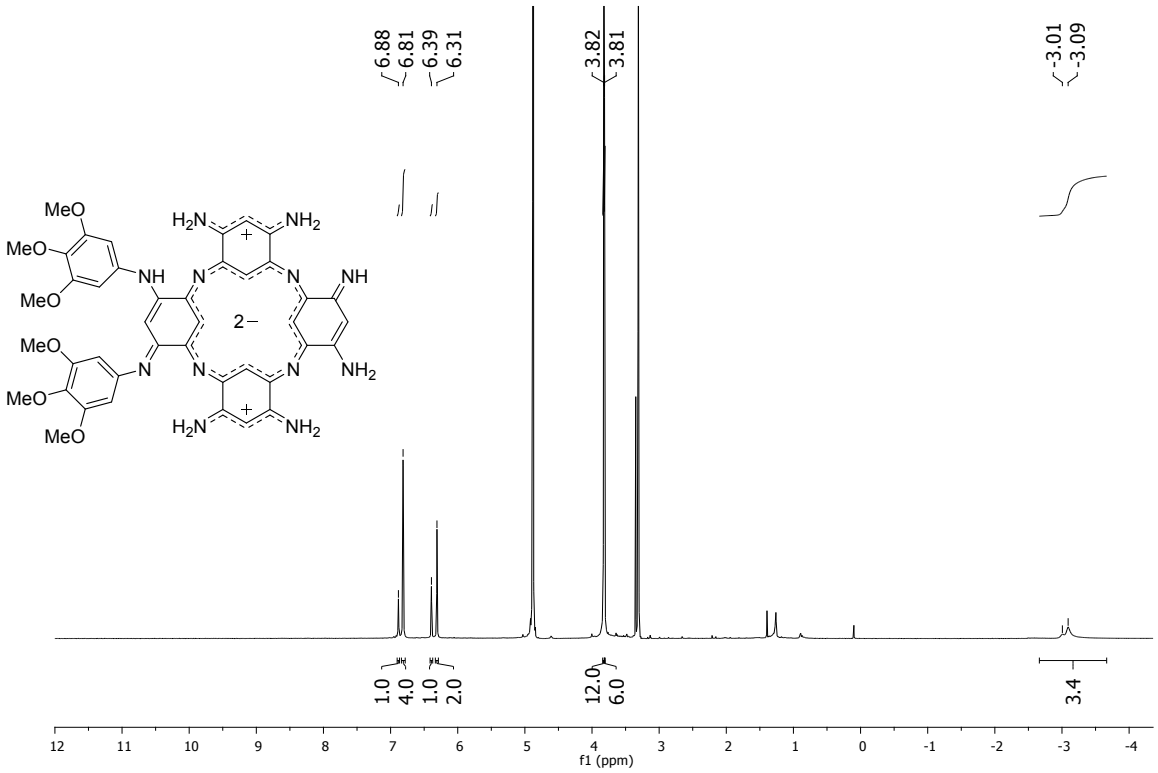


Figure S 5. ^{1}H NMR (400 MHz, MeOD) for compound **1a**.

Compound 1ab

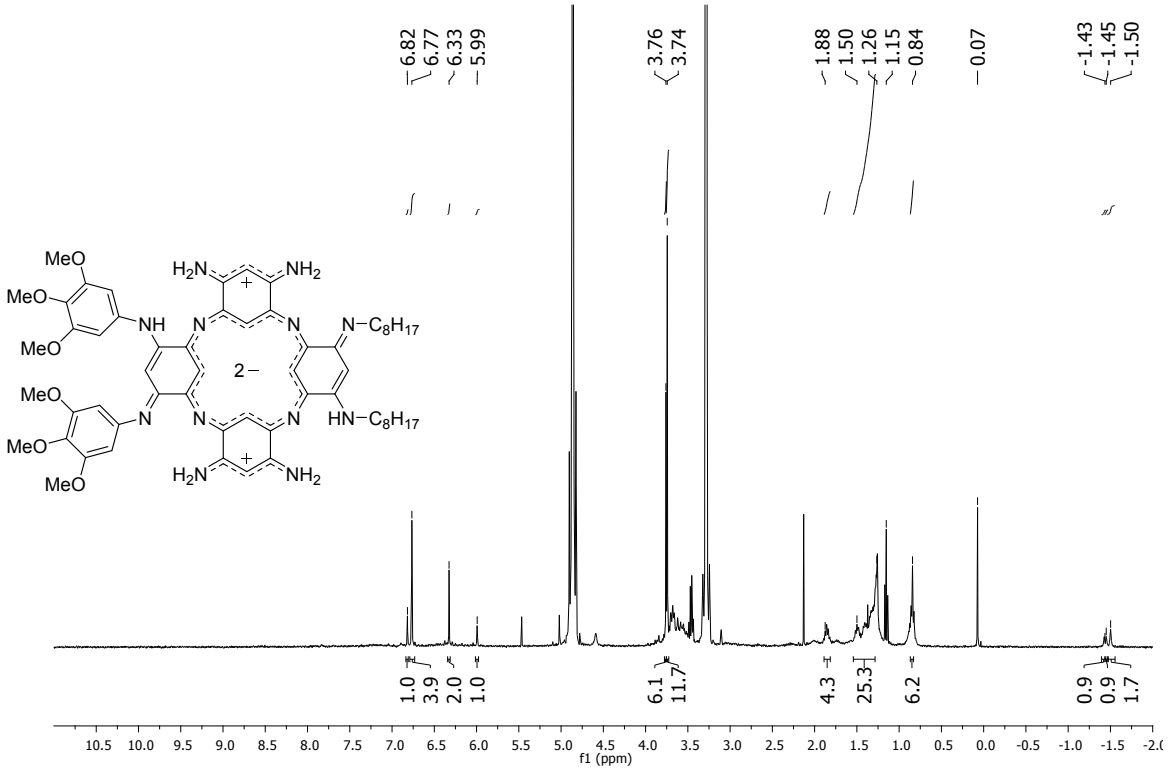


Figure S 6. ^{1}H NMR (400 MHz, MeOD) for compound **1ab**.

S-II. INFRARED SPECTRA

Compound 4a

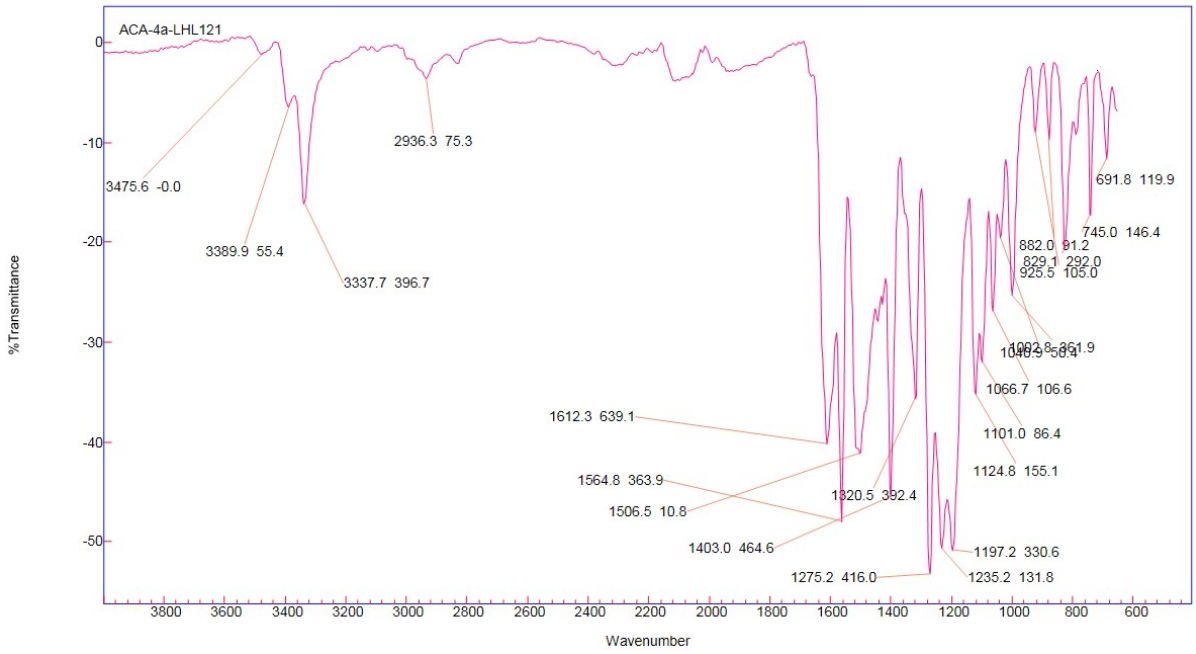


Figure S 7. Infrared spectrum (neat) of compound **4a.**

Compound 4ab

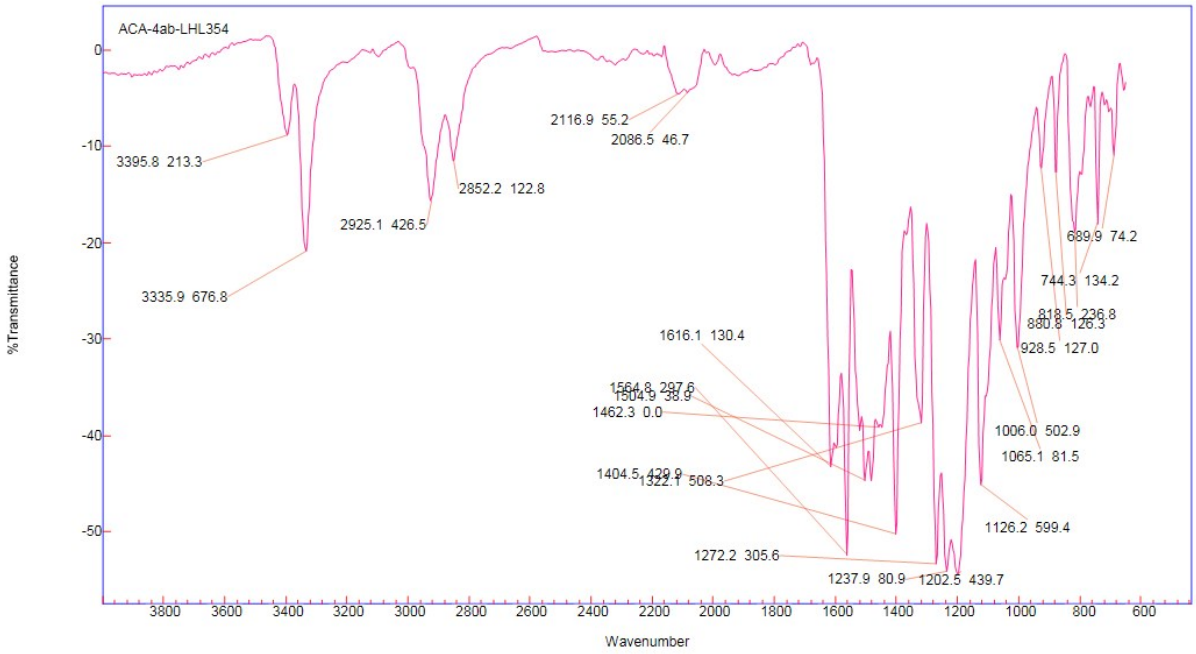


Figure S 8. Infrared spectrum (neat) of compound **4ab.**

Compound 1a

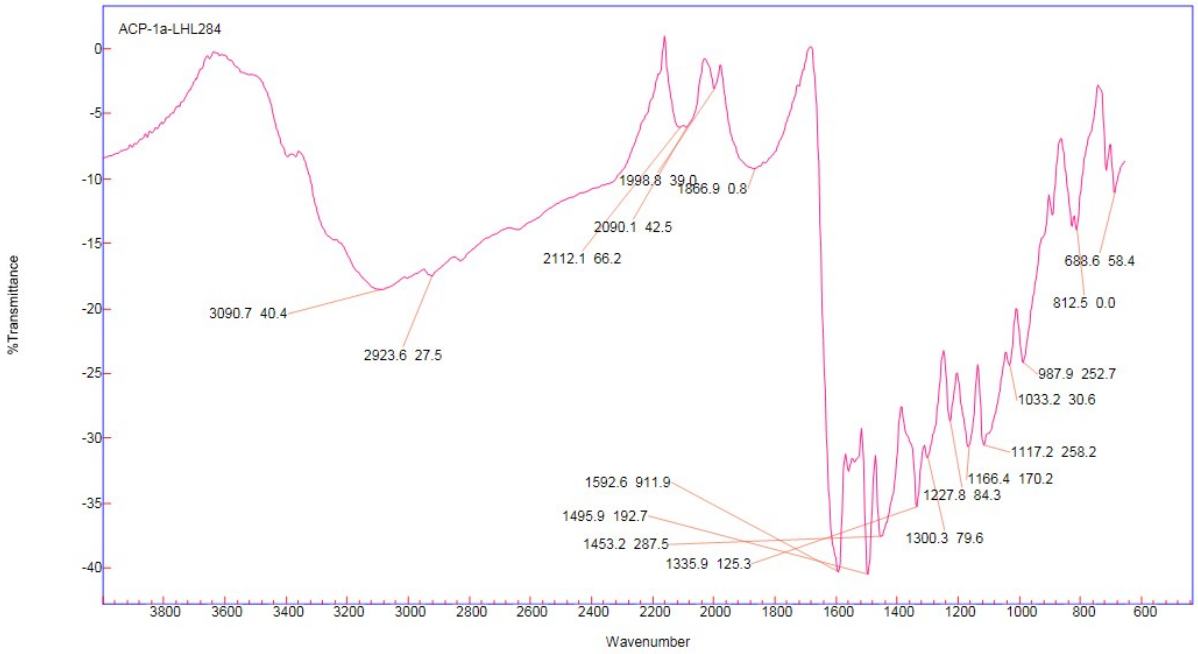


Figure S 9. Infrared spectrum (neat) of compound **1a.**

Compound 1ab

Figure S 10. Infrared spectrum (neat) of compound **1ab.**

S-III. HRMS ANALYSES

Compound 4a

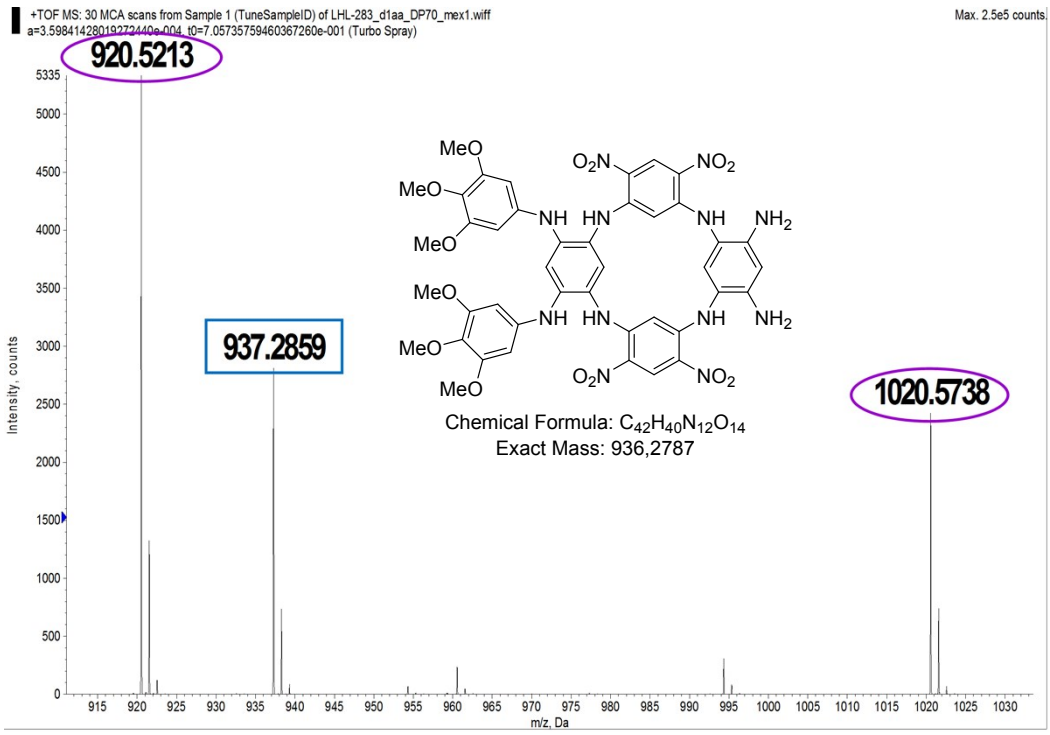


Figure S 11. HRMS spectrum of compound **4a**. Target ion is detected at m/z 937.2859 and calibration peaks are observed at m/z 920.5213 and m/z 1020.5738.

Compound 4ab

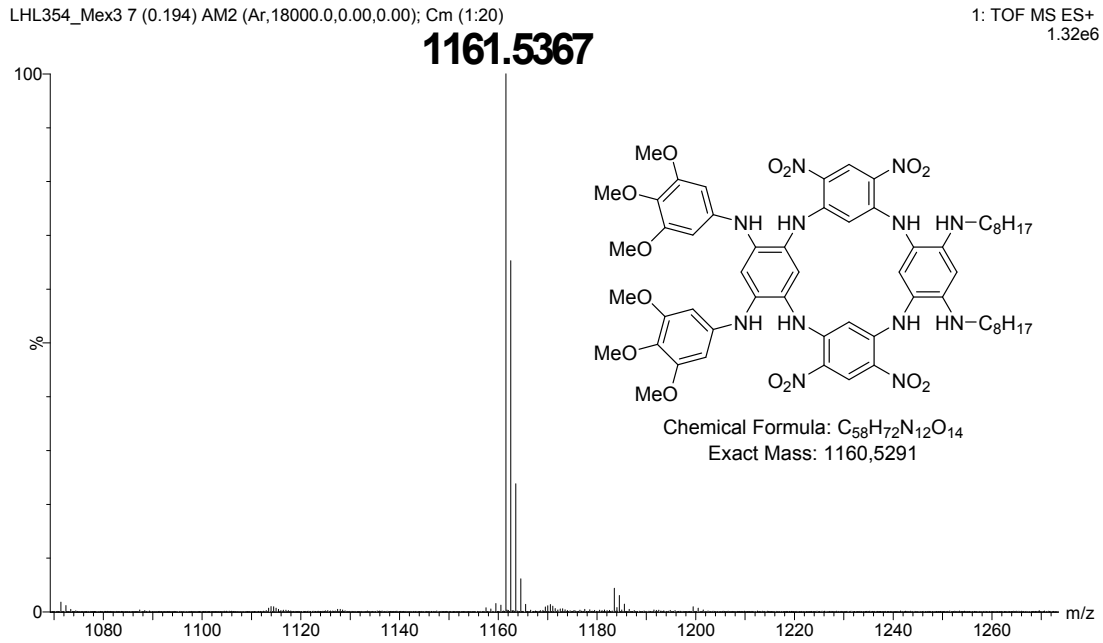


Figure S 12. HRMS spectrum of compound **4ab**.

Compound 1a

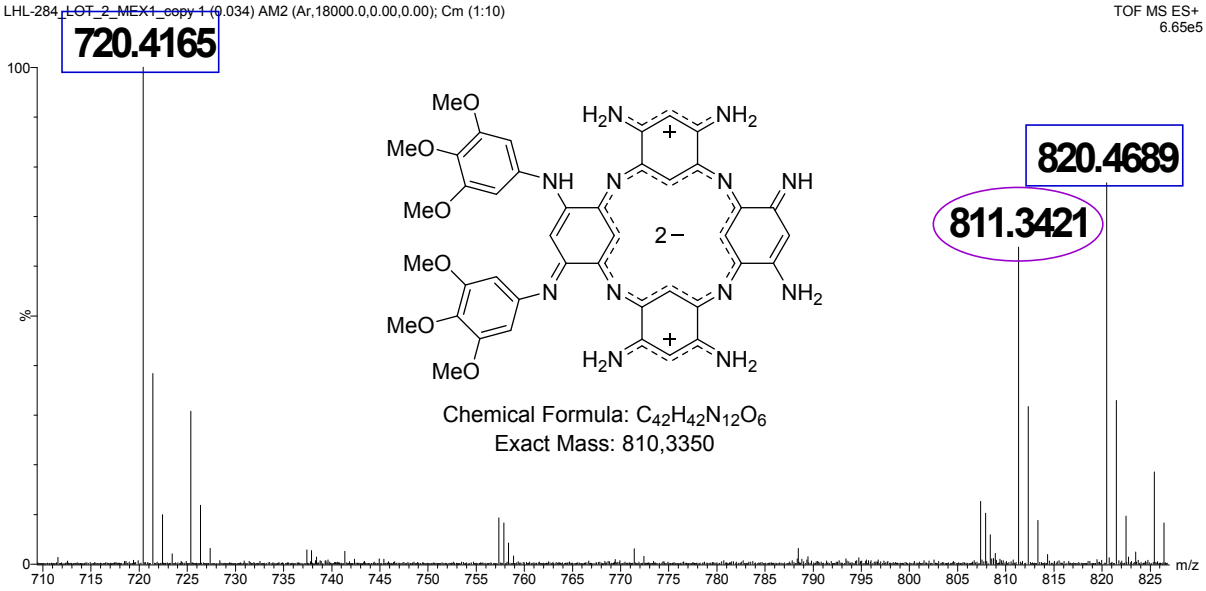


Figure S 13. HRMS spectrum of compound **1a**. Target ion is detected at m/z 811.3421 and calibration peaks are observed at m/z 720.4165 and m/z 820.4689.

Compound 1ab

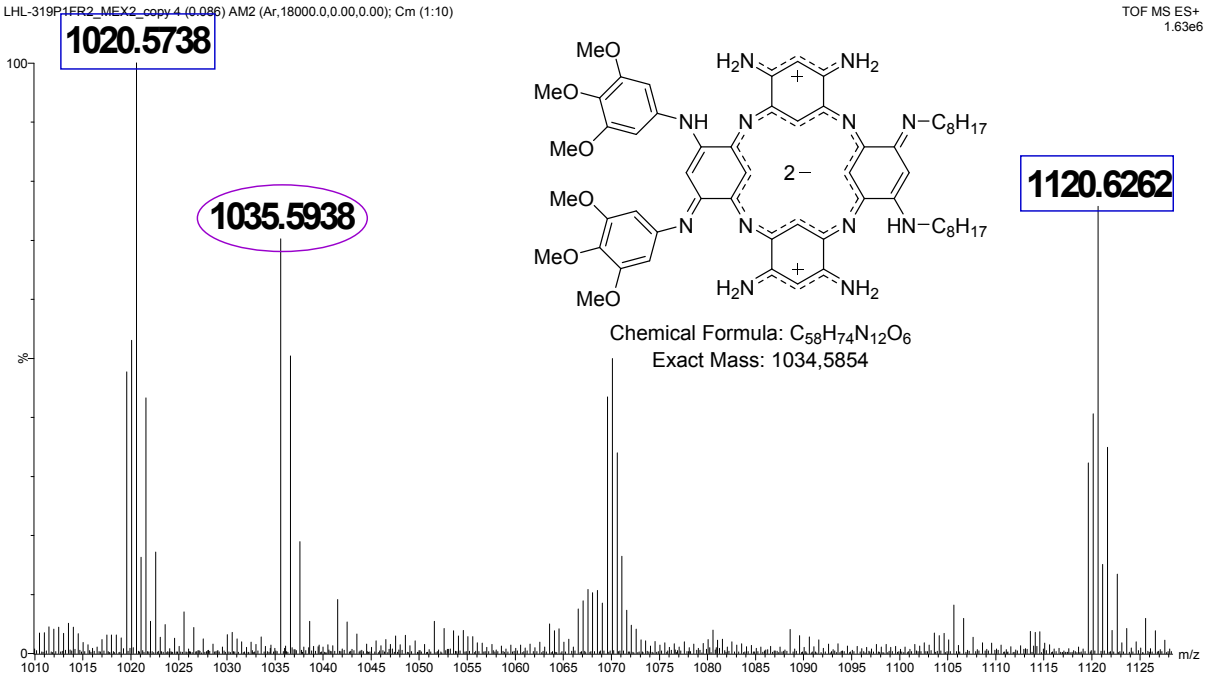
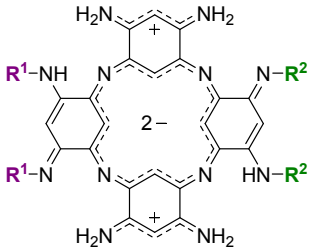


Figure S 14. HRMS spectrum of compound **1ab**. Target ion is detected at m/z 1035.5938 and calibration peaks are observed at m/z 1020.5738 and m/z 1120.6262.

S-IV. ELECTROCHEMICAL PROPERTIES

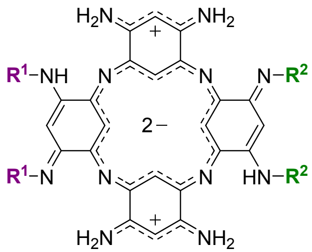


1a R^1 = $Ph(OMe)_3$ R^2 = H
1aa R^1 = $Ph(OMe)_3$ R^2 = $Ph(OMe)_3$
1ab R^1 = $Ph(OMe)_3$ R^2 = C_8H_{17}
1bb R^1 = C_8H_{17} R^2 = C_8H_{17}

Table S 1. Half-wave potential (V *vs*. Fc/Fc^+) and electrochemical gap (ΔE) of the compounds (recorded in DMF solutions containing 0.1 M of $[(^nBu_4N)PF_6]$ at a scan rate of 100 mV s^{-1}).

Compound	Reduction		Oxidation		ΔE
	$E_{1/2}$ red2	$E_{1/2}$ red1	$E_{1/2}$ ox1	$E_{1/2}$ ox2	
1a		–0.39	0.49	0.90	0.88
1aa	–1.36	–0.26	0.54	0.94	0.80
1ab	–1.27	–0.34	0.47		0.81
1bb [2]		–0.50	0.44		0.94

S-V. OPTICAL PROPERTIES



1	R^1 = H	R^2 = H
1a	R^1 = $Ph(OMe)_3$	R^2 = H
1aa	R^1 = $Ph(OMe)_3$	R^2 = $Ph(OMe)_3$
1ab	R^1 = $Ph(OMe)_3$	R^2 = C_8H_{17}
1bb	R^1 = C_8H_{17}	R^2 = C_8H_{17}

Table S 2. Optical properties of ACPs in basic (0.1 M DBU), neutral or acidic (0.1 M TFA) MeOH, DMF and DMSO.

Dye	MeOH			DMF			DMSO		
	Solvent only	TFA	DBU	Solvent only	TFA	DBU	Solvent only	TFA	DBU
	λ_{abs} (nm) *ε (M^{-1} cm^{-1})*	λ_{abs} (nm) *ε (M^{-1} cm^{-1})*	λ_{abs} (nm) *ε (M^{-1} cm^{-1})*	λ_{abs} (nm) *ε (M^{-1} cm^{-1})*	λ_{abs} (nm) *ε (M^{-1} cm^{-1})*	λ_{abs} (nm) *ε (M^{-1} cm^{-1})*	λ_{abs} (nm) *ε (M^{-1} cm^{-1})*	λ_{abs} (nm) *ε (M^{-1} cm^{-1})*	λ_{abs} (nm) *ε (M^{-1} cm^{-1})*
1	877 *5600*	888 *8000*	877 *3500*	882 *3600*	882 *7800*	892 *4000*	882 *6800*	882 *7200*	892 *3700*
1a	909 *18300*	910 *19800*	889 *12000*	877 *12500*	910 *20600*	754 *9200*	900 *14900*	910 *20900*	819 *9000*
1aa	938 *19900*	941 *21200*	807 *840*	851 *10800*	947 *20800*	761 *10700*	900 *8400*	944 *21500*	770 *13600*
1ab	883 *11700*	912 *13700*	871 *11000*	883 *12100*	913 *13300*	824 *6400*	898 *12300*	915 *13100*	820 *11100*
1bb	893 *13900*	894 *14500*	895 *11300*	893 *11900*	895 *14400*	864 *5300*	896 *14200*	897 *14900*	874 *6900*

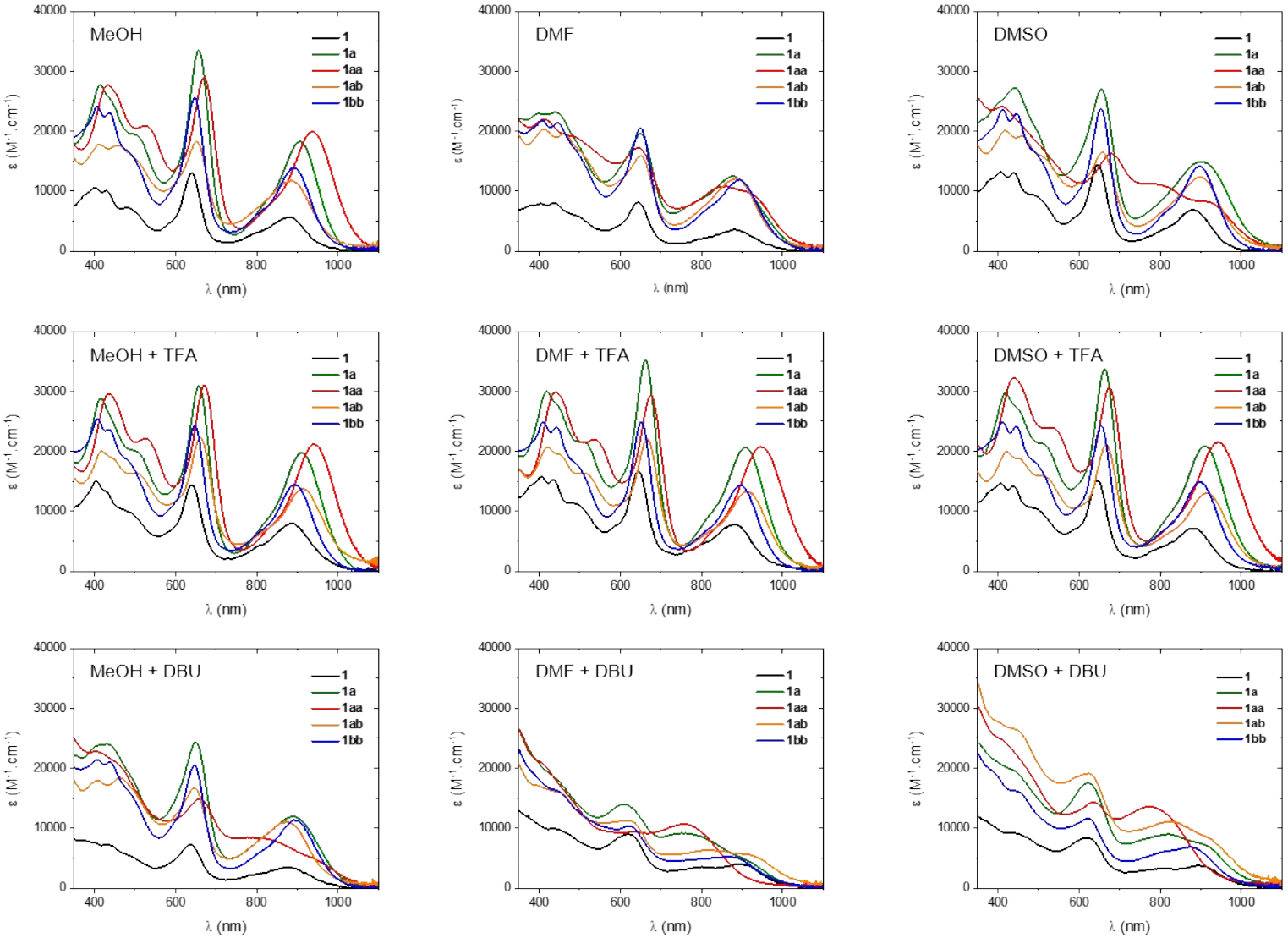


Figure S 15. Solvatochromism and pH-dependent absorption spectra of ACPs in basic (0.1 M DBU), neutral or acidic (0.1 M TFA) MeOH, DMF and DMSO.

Table S 3. Optical gaps (eV) determined from the slope intersect of the low-energy absorption band with the x-axis.

Dye	DMF		DMSO		MeOH	
	+ TFA	+ DBU	+ TFA	+ DBU	+ TFA	+ DBU
1a	1.23	1.23	1.22	1.22	1.23	1.23
1aa	1.16	1.35	1.16	1.31	1.18	1.16
1ab	1.22	1.18	1.22	1.18	1.21	1.26
1bb	1.26	1.23	1.25	1.25	1.26	1.25

S-VI. THEORETICAL CALCULATIONS

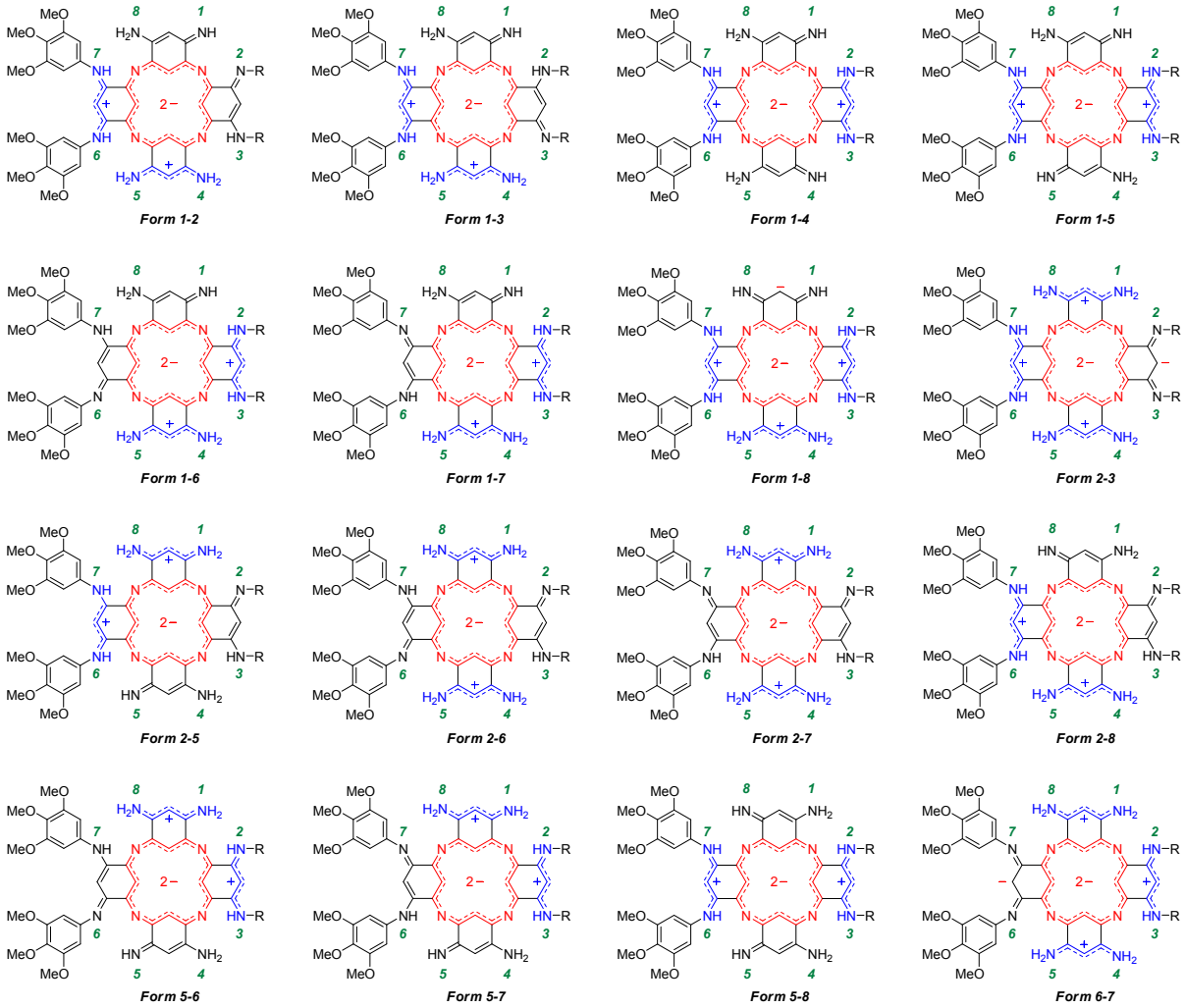


Figure S 16. Selected limit structures of azacalixphyrins **1a** (R = H) and **1ab** (R = C_8H_{17}). Tautomers denomination depends on the position of the two imine functions. Tautomers equivalent by symmetry are not shown.

S-VII. REFERENCES

1. L. Lavaud, S. Pascal, K. Metwally, D. Gasteau, A. Da Silva, Z. Chen, M. Elhabiri, G. Canard, D. Jacquemin and O. Siri, *Chem. Commun.*, 2018, **54**, 12365-12368.
2. Z. Chen, R. Haddoub, J. Mahé, G. Marchand, D. Jacquemin, J. Andeme Edzang, G. Canard, D. Ferry, O. Grauby, A. Ranguis and O. Siri, *Chem. Eur. J.*, 2016, **22**, 17820-17832.
3. N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877-910.