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ESI for Effects of Chemical Substitutions on the Properties of Azacalixphyrins: a First-principles Study†

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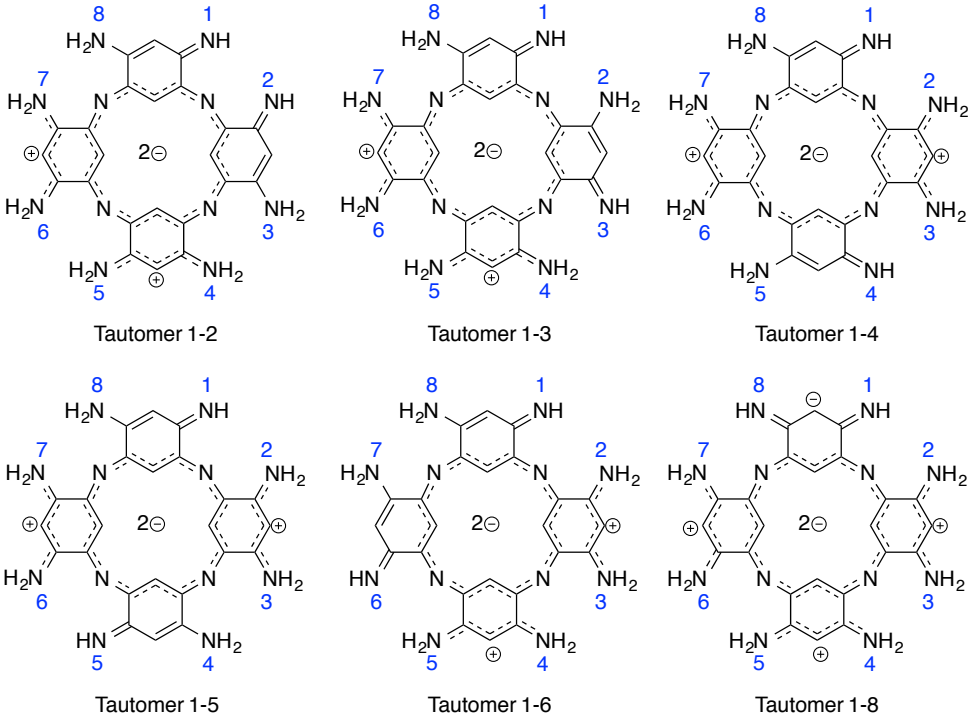
S1 Tautomers of 1



Scheme 1 Representation of the different tautomers of **1** .

S2 Absorption Spectra obtained with the B3LYP method

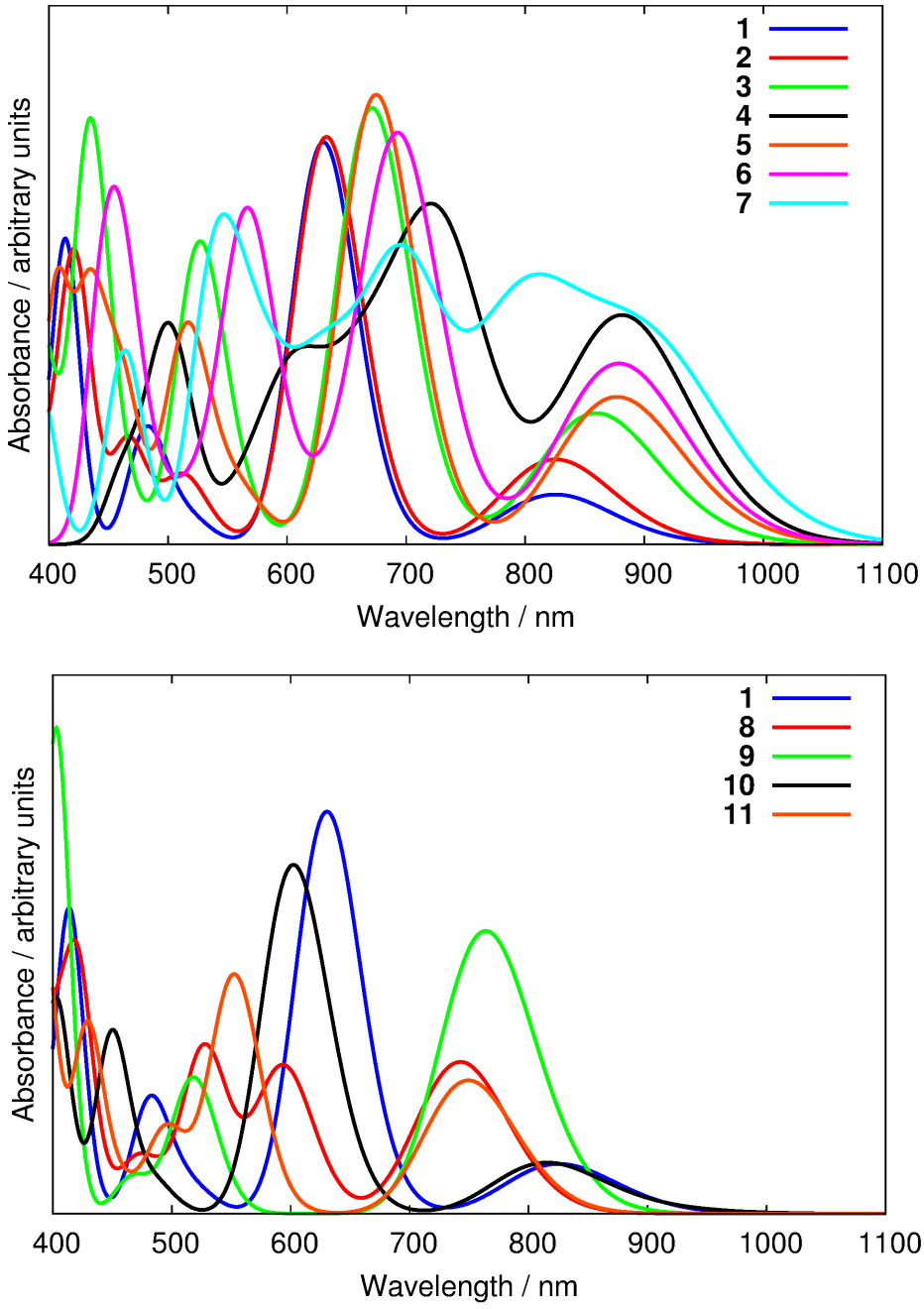


Fig. S-1 Absorption spectra of the $2H^+$ forms of the ACPs. The curves result from the convolution of the vertical excitation energies with a Gaussian function presenting a half-width at half-height of 0.1 eV. All curves have been obtained using the B3LYP functional.

S3 Transition energies and oscillator strengths obtained by TD-DFT

S3.1 Diprotonated derivatives

	1	**2**	**3**	**4**	**5**	**6**
$S_1 \leftarrow S_0$	1.45 (0.21)	1.39 (0.37)	1.39 (0.43)	1.38 (0.55)	1.34 (0.49)	1.36 (0.50)
$S_2 \leftarrow S_0$	1.45 (0.21)	1.48 (0.18)	1.41 (0.25)	1.42 (0.25)	1.41 (0.18)	1.40 (0.24)
$S_3 \leftarrow S_0$	2.00 (0.64)	1.98 (0.77)	1.94 (0.76)	1.93 (0.87)	1.91 (0.54)	1.92 (0.74)
$S_4 \leftarrow S_0$	2.00 (0.63)	2.08 (0.48)	1.95 (0.45)	1.93 (0.37)	1.93 (0.69)	1.93 (0.43)
$S_5 \leftarrow S_0$	2.68 (0.16)	2.66 (0.19)	2.49 (0.02)	2.32 (0.04)	2.51 (0.28)	2.43 (0.04)

	7	**8**	**9**	**10**	**11**
$S_1 \leftarrow S_0$	1.36 (0.35)	1.51 (0.51)	1.43 (0.51)	1.39 (0.35)	1.43 (0.57)
$S_2 \leftarrow S_0$	1.37 (0.51)	1.62 (0.30)	1.43 (0.51)	2.07 (0.44)	2.24 (0.91)
$S_3 \leftarrow S_0$	1.89 (0.83)	2.18 (0.50)	2.66 (0.19)	2.09 (0.90)	2.71 (0.35)
$S_4 \leftarrow S_0$	1.94 (0.16)	2.57 (0.50)	2.67 (0.19)	2.78 (0.09)	2.95 (0.01)
$S_5 \leftarrow S_0$	2.21 (0.02)	2.86 (0.16)	2.68 (0.20)	2.91 (0.03)	2.96 (0.02)

Table S-1 First five dipole-allowed lowest-lying (singlet) vertical excitation energies (in eV) and corresponding oscillator strength value (in parentheses), for all diprotonated dicationic azacalixphyrin compounds studied here. Only excitations with oscillator strengths $\geq$ 0.01 have been considered. All values have been obtained with the CAM-B3LYP functional.

	1	**2**	**3**	**4**	**5**	**6**
$S_1 \leftarrow S_0$	1.50 (0.05)	1.50 (0.05)	1.44 (0.19)	1.40 (0.36)	1.41 (0.24)	1.41 (0.27)
$S_2 \leftarrow S_0$	1.50 (0.05)	1.94 (0.52)	1.45 (0.07)	1.43 (0.08)	1.42 (0.04)	1.43 (0.08)
$S_3 \leftarrow S_0$	1.97 (0.39)	1.99 (0.29)	1.84 (0.65)	1.69 (0.55)	1.83 (0.62)	1.78 (0.27)
$S_4 \leftarrow S_0$	1.97 (0.39)	2.32 (0.02)	1.86 (0.19)	1.80 (0.12)	1.84 (0.25)	1.79 (0.52)
$S_5 \leftarrow S_0$	2.40 (0.05)	2.41 (0.07)	2.27 (0.10)	1.86 (0.07)	2.21 (0.10)	1.96 (0.01)

	7	**8**	**9**	**10**	**11**
$S_1 \leftarrow S_0$	1.33 (0.13)	1.66 (0.22)	1.62 (0.27)	1.38 (0.01)	1.65 (0.26)
$S_2 \leftarrow S_0$	1.39 (0.26)	1.70 (0.08)	1.62 (0.27)	1.52 (0.10)	2.24 (0.46)
$S_3 \leftarrow S_0$	1.54 (0.41)	2.09 (0.28)	2.37 (0.09)	1.99 (0.26)	2.50 (0.17)
$S_4 \leftarrow S_0$	1.60 (0.05)	2.35 (0.32)	2.37 (0.09)	1.99 (0.26)	2.71 (0.05)
$S_5 \leftarrow S_0$	1.78 (0.52)	2.53 (0.02)	2.43 (0.10)	2.08 (0.47)	2.89 (0.35)

Table S-2 First five dipole-allowed lowest-lying (singlet) vertical excitation energies (in eV) and corresponding oscillator strength value (in parentheses), for all diprotonated dicationic azacalixphyrin compounds studied here. Only excitations with oscillator strengths $\geq$ 0.01 have been considered. All values have been obtained with the B3LYP functional.

S3.2 Neutral derivatives

		Tautomer									
		1-2	1-3	1-4	1-5	1-6	1-7	1-8	2-3	2-6	2-7
1	$S_1 \leftarrow S_0$	1.54 (0.16)	1.47 (0.12)	1.42 (0.24)	1.27 (0.20)	1.53 (0.18)	*=1-3*	0.67 (0.08)	*=1-8*	*=1-5*	*=1-4*
	$S_2 \leftarrow S_0$	1.62 (0.01)	1.82 (0.06)	1.48 (0.02)	1.48 (0.07)	2.27 (0.25)	*=1-3*	0.83 (0.01)	*=1-8*	*=1-5*	*=1-4*
	$S_3 \leftarrow S_0$	2.26 (0.23)	2.29 (0.22)	2.43 (0.13)	2.40 (0.28)	2.30 (0.14)	*=1-3*	1.40 (0.06)	*=1-8*	*=1-5*	*=1-4*
	$S_4 \leftarrow S_0$	2.53 (0.01)	2.52 (0.25)	2.52 (0.21)	2.50 (0.05)	2.70 (0.05)	*=1-3*	1.58 (0.01)	*=1-8*	*=1-5*	*=1-4*
	$S_5 \leftarrow S_0$	2.64 (0.36)	2.70 (0.03)	2.54 (0.03)	2.73 (0.01)	2.86 (0.01)	*=1-3*	2.09 (0.31)	*=1-8*	*=1-5*	*=1-4*
2	$S_1 \leftarrow S_0$	1.50 (0.12)	1.49 (0.21)	1.38 (0.35)	1.26 (0.34)	1.54 (0.25)	1.51 (0.10)	0.59 (0.06)	0.73 (0.06)	1.33 (0.21)	1.57 (0.02)
	$S_2 \leftarrow S_0$	1.72 (0.08)	1.78 (0.04)	2.39 (0.36)	1.55 (0.04)	2.26 (0.34)	1.97 (0.09)	0.62 (0.01)	1.38 (0.07)	1.58 (0.07)	1.67 (0.23)
	$S_3 \leftarrow S_0$	2.27 (0.24)	2.29 (0.23)	2.68 (0.13)	2.34 (0.33)	2.35 (0.16)	2.32 (0.31)	1.40 (0.05)	1.62 (0.09)	2.35 (0.52)	2.50 (0.53)
	$S_4 \leftarrow S_0$	2.53 (0.37)	2.46 (0.40)	2.70 (0.01)	2.66 (0.06)	2.79 (0.03)	2.49 (0.22)	1.68 (0.05)	2.03 (0.45)	2.66 (0.06)	2.66 (0.03)
	$S_5 \leftarrow S_0$	2.65 (0.04)	2.79 (0.03)	2.90 (0.03)	2.77 (0.20)	2.88 (0.01)	2.75 (0.06)	1.95 (0.17)	2.13 (0.10)	2.75 (0.13)	2.77 (0.06)
3	$S_1 \leftarrow S_0$	1.42 (0.23)	1.42 (0.25)	1.27 (0.48)	1.16 (0.48)	1.45 (0.35)	1.40 (0.14)	0.63 (0.07)	0.66 (0.07)	1.33 (0.19)	1.57 (0.03)
	$S_2 \leftarrow S_0$	1.58 (0.03)	1.78 (0.10)	1.47 (0.01)	1.46 (0.06)	1.67 (0.01)	1.78 (0.11)	0.80 (0.02)	1.34 (0.04)	1.58 (0.07)	1.61 (0.22)
	$S_3 \leftarrow S_0$	2.14 (0.28)	2.20 (0.11)	2.35 (0.15)	2.21 (0.01)	2.15 (0.25)	2.19 (0.44)	1.31 (0.16)	1.58 (0.29)	2.20 (0.66)	2.32 (0.75)
	$S_4 \leftarrow S_0$	2.41 (0.42)	2.40 (0.46)	2.41 (0.05)	2.31 (0.16)	2.26 (0.20)	2.34 (0.11)	1.57 (0.03)	1.91 (0.06)	2.51 (0.08)	2.45 (0.01)
	$S_5 \leftarrow S_0$	2.43 (0.03)	2.48 (0.14)	2.49 (0.05)	2.49 (0.05)	2.56 (0.06)	2.59 (0.03)	1.96 (0.22)	1.94 (0.42)	2.62 (0.07)	2.55 (0.01)
4	$S_1 \leftarrow S_0$	1.40 (0.29)	1.38 (0.34)	1.24 (0.60)	1.11 (0.61)	1.42 (0.43)	1.39 (0.17)	0.62 (0.07)	0.65 (0.07)	1.32 (0.18)	1.55 (0.01)
	$S_2 \leftarrow S_0$	1.58 (0.02)	1.76 (0.12)	2.31 (0.07)	1.44 (0.06)	1.66 (0.01)	1.80 (0.10)	0.79 (0.02)	0.79 (0.01)	1.56 (0.08)	1.58 (0.22)
	$S_3 \leftarrow S_0$	2.07 (0.34)	2.11 (0.09)	2.36 (0.04)	2.16 (0.01)	2.06 (0.27)	2.14 (0.66)	1.28 (0.21)	1.30 (0.04)	2.09 (0.39)	2.17 (0.72)
	$S_4 \leftarrow S_0$	2.27 (0.04)	2.24 (0.24)	2.43 (0.08)	2.27 (0.07)	2.22 (0.22)	2.27 (0.04)	1.56 (0.04)	1.52 (0.45)	2.13 (0.55)	2.21 (0.01)
	$S_5 \leftarrow S_0$	2.36 (0.57)	2.39 (0.44)	2.56 (0.28)	2.42 (0.05)	2.38 (0.16)	2.43 (0.17)	1.91 (0.17)	1.81 (0.30)	2.24 (0.01)	2.34 (0.40)
5	$S_1 \leftarrow S_0$	1.39 (0.26)	1.42 (0.25)	1.23 (0.46)	1.08 (0.48)	1.45 (0.36)	1.35 (0.19)	0.66 (0.08)	0.86 (0.01)	1.36 (0.19)	1.60 (0.23)
	$S_2 \leftarrow S_0$	1.58 (0.04)	1.82 (0.15)	1.38 (0.01)	1.37 (0.08)	1.66 (0.03)	1.66 (0.08)	0.92 (0.01)	0.87 (0.05)	1.57 (0.07)	2.28 (0.82)
	$S_3 \leftarrow S_0$	2.15 (0.28)	2.23 (0.13)	2.25 (0.04)	2.18 (0.34)	2.18 (0.34)	2.12 (0.46)	1.26 (0.23)	1.36 (0.02)	2.19 (0.78)	2.53 (0.04)
	$S_4 \leftarrow S_0$	2.40 (0.43)	2.42 (0.44)	2.29 (0.09)	2.26 (0.14)	2.26 (0.14)	2.31 (0.17)	1.50 (0.02)	1.59 (0.42)	2.55 (0.15)	2.67 (0.01)
	$S_5 \leftarrow S_0$	2.65 (0.07)	2.59 (0.15)	2.43 (0.13)	2.59 (0.06)	2.59 (0.06)	2.48 (0.04)	1.96 (0.24)	1.92 (0.04)	2.67 (0.07)	2.73 (0.09)
6	$S_1 \leftarrow S_0$	1.41 (0.25)	1.42 (0.29)	1.26 (0.54)	1.14 (0.54)	1.46 (0.39)	1.40 (0.16)	0.63 (0.07)	0.68 (0.07)	1.32 (0.19)	1.57 (0.04)
	$S_2 \leftarrow S_0$	1.60 (0.03)	1.76 (0.10)	1.47 (0.01)	1.44 (0.06)	1.68 (0.01)	1.79 (0.12)	0.79 (0.02)	0.81 (0.01)	1.58 (0.07)	1.60 (0.20)
	$S_3 \leftarrow S_0$	2.12 (0.33)	2.19 (0.09)	2.34 (0.14)	2.17 (0.01)	2.15 (0.28)	2.18 (0.51)	1.31 (0.18)	1.33 (0.04)	2.18 (0.74)	2.29 (0.83)
	$S_4 \leftarrow S_0$	2.38 (0.48)	2.38 (0.51)	2.40 (0.03)	2.31 (0.14)	2.26 (0.23)	2.34 (0.10)	1.57 (0.04)	1.56 (0.34)	2.28 (0.01)	2.43 (0.01)
	$S_5 \leftarrow S_0$	2.41 (0.01)	2.45 (0.17)	2.48 (0.07)	2.45 (0.05)	2.56 (0.05)	2.58 (0.10)	1.95 (0.22)	1.89 (0.10)	2.48 (0.08)	2.50 (0.02)
7	$S_1 \leftarrow S_0$	1.41 (0.18)	1.41 (0.31)	1.29 (0.53)	1.17 (0.53)	1.45 (0.39)	1.44 (0.14)	0.59 (0.06)	0.58 (0.11)	1.25 (0.18)	1.54 (0.06)
	$S_2 \leftarrow S_0$	1.69 (0.09)	1.74 (0.07)	2.31 (0.14)	1.49 (0.04)	2.06 (0.24)	1.86 (0.13)	0.67 (0.02)	0.78 (0.01)	1.56 (0.08)	1.59 (0.20)
	$S_3 \leftarrow S_0$	2.13 (0.31)	2.12 (0.08)	2.45 (0.01)	2.26 (0.01)	2.25 (0.19)	2.18 (0.55)	1.34 (0.13)	1.23 (0.06)	2.10 (0.75)	2.14 (0.34)
	$S_4 \leftarrow S_0$	2.31 (0.06)	2.26 (0.15)	2.58 (0.09)	2.27 (0.14)	2.41 (0.12)	2.30 (0.06)	1.62 (0.06)	1.54 (0.28)	2.22 (0.05)	2.24 (0.18)
	$S_5 \leftarrow S_0$	2.37 (0.43)	2.40 (0.51)	2.64 (0.22)	2.56 (0.05)	2.63 (0.12)	2.46 (0.19)	1.91 (0.34)	1.79 (0.01)	2.44 (0.09)	2.85 (0.31)
8	$S_1 \leftarrow S_0$	1.65 (0.21)	1,66 (0.21)	1.56 (0.26)	1.43 (0.26)	1.65 (0.23)	1.64 (0.20)	0.67 (0.07)	0.43 (0.03)	1.33 (0.29)	1.37 (0.29)
	$S_2 \leftarrow S_0$	1.98 (0.01)	2.02 (0.01)	2.48 (0.37)	1.83 (0.04)	2.00 (0.02)	2.10 (0.04)	1.56 (0.03)	1.35 (0.09)	1.66 (0.02)	1.66 (0.01)
	$S_3 \leftarrow S_0$	2.45 (0.17)	2.53 (0.20)	2.63 (0.04)	2.49 (0.42)	2.32 (0.21)	2.34 (0.18)	1.90 (0.15)	1.71 (0.01)	2.54 (0.04)	2.27 (0.01)
	$S_4 \leftarrow S_0$	2.65 (0.01)	2.58 (0.32)	2.73 (0.03)	2.66 (0.01)	2.68 (0.15)	2.73 (0.03)	2.02 (0.23)	2.04 (0.01)	2.55 (0.29)	2.56 (0.02)
	$S_5 \leftarrow S_0$	2.69 (0.40)	2.74 (0.03)	2.77 (0.12)	2.89 (0.04)	2.76 (0.01)	2.80 (0.26)	2.36 (0.22)	2.17 (0.30)	3.00 (0.03)	2.57 (0.29)
9	$S_1 \leftarrow S_0$	1.59 (0.26)	1.60 (0.26)	1.34 (0.26)	1.26 (0.28)	1.61 (0.29)	*=1-3*	0.46 (0.04)	*=1-8*	*=1-5*	*=1-4*
	$S_2 \leftarrow S_0$	2.24 (0.01)	2.26 (0.05)	1.92 (0.01)	1.88 (0.03)	2.16 (0.06)	*=1-3*	1.32 (0.09)	*=1-8*	*=1-5*	*=1-4*
	$S_3 \leftarrow S_0$	2.62 (0.24)	2.53 (0.20)	2.41 (0.15)	2.37 (0.16)	2.50 (0.16)	*=1-3*	1.80 (0.12)	*=1-8*	*=1-5*	*=1-4*
	$S_4 \leftarrow S_0$	2.70 (0.10)	2.78 (0.06)	2.50 (0.05)	2.55 (0.03)	2.76 (0.05)	*=1-3*	1.91 (0.08)	*=1-8*	*=1-5*	*=1-4*
	$S_5 \leftarrow S_0$	2.79 (0.01)	2.83 (0.01)	2.61 (0.04)	2.70 (0.22)	2.90 (0.01)	*=1-3*	2.13 (0.30)	*=1-8*	*=1-5*	*=1-4*
10	$S_1 \leftarrow S_0$	1.53 (0.07)	1.46 (0.11)	1.68 (0.25)	1.48 (0.18)	1.61 (0.12)	1.54 (0.07)	0.98 (0.01)	0.74 (0.09)	1.29 (0.15)	1.39 (0.19)
	$S_2 \leftarrow S_0$	1.69 (0.07)	1.68 (0.03)	2.53 (0.34)	1.65 (0.09)	1.73 (0.05)	1.94 (0.07)	1.50 (0.01)	0.98 (0.01)	1.52 (0.10)	1.43 (0.03)
	$S_3 \leftarrow S_0$	2.27 (0.26)	2.20 (0.12)	2.64 (0.28)	2.45 (0.36)	2.32 (0.17)	2.37 (0.29)	1.77 (0.03)	1.46 (0.05)	2.31 (0.02)	2.13 (0.02)
	$S_4 \leftarrow S_0$	2.54 (0.03)	2.39 (0.15)	2.87 (0.01)	2.71 (0.29)	2.42 (0.26)	2.64 (0.27)	2.08 (0.01)	2.27 (0.33)	2.49 (0.33)	2.27 (0.04)
	$S_5 \leftarrow S_0$	2.64 (0.30)	2.47 (0.24)	3.01 (0.05)	2.97 (0.02)	2.74 (0.08)	2.72 (0.04)	2.09 (0.03)	2.27 (0.39)	2.89 (0.14)	2.59 (0.35)
11	$S_1 \leftarrow S_0$	1.69 (0.14)	1.69 (0.15)	1.87 (0.26)	1.68 (0.25)	1.76 (0.18)	1.75 (0.14)	1.24 (0.01)	0.48 (0.04)	1.37 (0.25)	1.39 (0.26)
	$S_2 \leftarrow S_0$	2.03 (0.03)	2.35 (0.10)	1.96 (0.01)	1.93 (0.07)	2.01 (0.03)	2.14 (0.08)	1.84 (0.01)	1.40 (0.08)	1.66 (0.03)	1.64 (0.01)
	$S_3 \leftarrow S_0$	2.48 (0.31)	2.48 (0.22)	2.73 (0.49)	2.65 (0.43)	2.50 (0.36)	2.53 (0.32)	2.13 (0.16)	2.36 (0.33)	2.37 (0.05)	2.38 (0.05)
	$S_4 \leftarrow S_0$	2.64 (0.06)	2.63 (0.23)	2.74 (0.33)	2.84 (0.37)	2.74 (0.01)	2.84 (0.06)	2.50 (0.01)	2.41 (0.30)	2.67 (0.29)	2.66 (0.07)
	$S_5 \leftarrow S_0$	2.68 (0.02)	2.81 (0.01)	3.25 (0.04)	3.30 (0.01)	2.84 (0.07)	2.87 (0.01)	2.64 (0.46)	2.54 (0.12)	2.86 (0.08)	2.69 (0.21)

Table S-3 First five dipole-allowed lowest-lying (singlet) vertical excitation energies (in eV) and corresponding oscillator strength values (in parentheses), for all tautomers of the neutral ACP derivatives. Only excitations with oscillator strengths ≥ 0.01 have been considered. All values have been obtained with the CAM-B3LYP functional.

		Tautomer									
		1-2	1-3	1-4	1-5	1-6	1-7	1-8	2-3	2-6	2-7
1	$S_1 \leftarrow S_0$	1.22 (0.01)	1.29 (0.05)	1.30 (0.12)	1.21 (0.08)	1.38 (0.10)	*=1-3*	0.62 (0.01)	*=1-8*	*=1-5*	*=1-4*
	$S_2 \leftarrow S_0$	1.45 (0.09)	1.56 (0.05)	1.36 (0.02)	1.48 (0.09)	1.39 (0.01)	*=1-3*	0.79 (0.07)	*=1-8*	*=1-5*	*=1-4*
	$S_3 \leftarrow S_0$	2.02 (0.18)	1.92 (0.07)	1.85 (0.07)	1.86 (0.05)	1.91 (0.19)	*=1-3*	1.37 (0.03)	*=1-8*	*=1-5*	*=1-4*
	$S_4 \leftarrow S_0$	2.24 (0.28)	1.99 (0.09)	2.23 (0.25)	2.16 (0.23)	2.09 (0.10)	*=1-3*	1.68 (0.01)	*=1-8*	*=1-5*	*=1-4*
	$S_5 \leftarrow S_0$	2.45 (0.01)	2.21 (0.16)	2.33 (0.07)	2.43 (0.03)	2.38 (0.05)	*=1-3*	1.88 (0.21)	*=1-8*	*=1-5*	*=1-4*
2	$S_1 \leftarrow S_0$	1.29 (0.01)	1.33 (0.09)	1.32 (0.23)	1.26 (0.17)	1.43 (0.15)	1.34 (0.06)	0.49 (0.01)	0.66 (0.01)	1.30 (0.10)	1.43 (0.03)
	$S_2 \leftarrow S_0$	1.45 (0.12)	1.58 (0.09)	1.91 (0.03)	1.52 (0.10)	1.46 (0.01)	1.62 (0.06)	0.74 (0.06)	0.79 (0.09)	1.55 (0.10)	1.44 (0.14)
	$S_3 \leftarrow S_0$	1.99 (0.18)	1.97 (0.16)	1.96 (0.05)	1.98 (0.05)	1.91 (0.22)	1.83 (0.02)	1.38 (0.03)	1.37 (0.04)	1.97 (0.02)	1.94 (0.02)
	$S_4 \leftarrow S_0$	2.16 (0.28)	2.03 (0.04)	2.16 (0.26)	2.12 (0.25)	1.92 (0.05)	1.90 (0.21)	1.56 (0.03)	1.54 (0.07)	2.11 (0.40)	1.98 (0.01)
	$S_5 \leftarrow S_0$	2.44 (0.06)	2.19 (0.23)	2.32 (0.13)	2.39 (0.05)	2.11 (0.02)	2.05 (0.01)	1.88 (0.20)	1.73 (0.02)	2.40 (0.11)	2.19 (0.41)
3	$S_1 \leftarrow S_0$	1.17 (0.01)	1.26 (0.13)	1.18 (0.31)	1.14 (0.25)	1.31 (0.23)	1.21 (0.05)	0.60 (0.02)	0.45 (0.01)	1.23 (0.09)	1.37 (0.08)
	$S_2 \leftarrow S_0$	1.33 (0.16)	1.52 (0.13)	1.31 (0.01)	1.40 (0.18)	1.74 (0.10)	1.49 (0.09)	0.74 (0.07)	0.67 (0.10)	1.53 (0.07)	1.40 (0.07)
	$S_3 \leftarrow S_0$	1.57 (0.01)	1.60 (0.02)	1.71 (0.06)	1.53 (0.01)	1.78 (0.10)	1.59 (0.03)	1.27 (0.11)	1.27 (0.02)	1.81 (0.04)	1.69 (0.03)
	$S_4 \leftarrow S_0$	1.84 (0.20)	1.83 (0.04)	1.78 (0.11)	1.81 (0.09)	1.88 (0.01)	1.73 (0.01)	1.44 (0.02)	1.43 (0.26)	1.91 (0.47)	1.78 (0.04)
	$S_5 \leftarrow S_0$	2.02 (0.31)	1.87 (0.01)	2.07 (0.07)	2.05 (0.09)	1.96 (0.19)	1.79 (0.33)	1.75 (0.13)	1.60 (0.04)	2.14 (0.09)	2.02 (0.46)
4	$S_1 \leftarrow S_0$	1.13 (0.04)	1.17 (0.22)	1.13 (0.44)	1.09 (0.36)	1.22 (0.25)	1.20 (0.08)	0.58 (0.03)	0.42 (0.01)	1.13 (0.06)	1.26 (0.05)
	$S_2 \leftarrow S_0$	1.26 (0.12)	1.43 (0.01)	1.67 (0.10)	1.36 (0.20)	1.35 (0.04)	1.39 (0.01)	0.73 (0.06)	0.58 (0.11)	1.49 (0.05)	1.27 (0.04)
	$S_3 \leftarrow S_0$	1.36 (0.14)	1.48 (0.18)	1.72 (0.10)	1.49 (0.01)	1.58 (0.02)	1.48 (0.10)	1.23 (0.15)	1.06 (0.03)	1.58 (0.09)	1.51 (0.10)
	$S_4 \leftarrow S_0$	1.68 (0.21)	1.63 (0.02)	1.86 (0.06)	1.75 (0.12)	1.62 (0.17)	1.68 (0.15)	1.42 (0.03)	1.17 (0.28)	1.68 (0.04)	1.53 (0.01)
	$S_5 \leftarrow S_0$	1.76 (0.04)	1.70 (0.04)	1.89 (0.02)	1.83 (0.02)	1.75 (0.02)	1.72 (0.41)	1.59 (0.05)	1.36 (0.03)	1.73 (0.33)	1.78 (0.02)
5	$S_1 \leftarrow S_0$	1.16 (0.03)	1.27 (0.16)	1.08 (0.27)	1.04 (0.20)	1.30 (0.17)	1.15 (0.05)	0.68 (0.02)	0.64 (0.07)	1.32 (0.09)	1.43 (0.14)
	$S_2 \leftarrow S_0$	1.34 (0.17)	1.52 (0.14)	1.20 (0.01)	1.33 (0.21)	1.37 (0.08)	1.15 (0.05)	0.75 (0.07)	1.20 (0.02)	1.52 (0.08)	1.45 (0.01)
	$S_3 \leftarrow S_0$	1.63 (0.02)	1.70 (0.02)	1.61 (0.22)	1.66 (0.13)	1.76 (0.15)	1.44 (0.09)	1.21 (0.15)	1.33 (0.36)	1.90 (0.08)	1.89 (0.08)
	$S_4 \leftarrow S_0$	1.85 (0.17)	1.84 (0.06)	2.08 (0.05)	2.05 (0.11)	1.80 (0.17)	1.56 (0.04)	1.37 (0.02)	1.64 (0.04)	1.94 (0.59)	1.89 (0.02)
	$S_5 \leftarrow S_0$	1.99 (0.36)	1.88 (0.03)	2.16 (0.05)	2.23 (0.06)	1.90 (0.01)	1.71 (0.31)	1.65 (0.02)	1.76 (0.04)	2.19 (0.11)	1.99 (0.63)
6	$S_1 \leftarrow S_0$	1.16 (0.01)	1.25 (0.13)	1.17 (0.38)	1.12 (0.28)	1.31 (0.26)	1.22 (0.05)	0.59 (0.03)	0.50 (0.01)	1.19 (0.08)	1.31 (0.09)
	$S_2 \leftarrow S_0$	1.30 (0.15)	1.48 (0.14)	1.31 (0.01)	1.37 (0.19)	1.38 (0.01)	1.49 (0.11)	0.74 (0.06)	0.65 (0.12)	1.52 (0.07)	1.38 (0.05)
	$S_3 \leftarrow S_0$	1.51 (0.04)	1.56 (0.04)	1.72 (0.05)	1.79 (0.12)	1.74 (0.09)	1.57 (0.03)	1.27 (0.13)	1.22 (0.03)	1.76 (0.05)	1.65 (0.03)
	$S_4 \leftarrow S_0$	1.79 (0.27)	1.80 (0.02)	1.77 (0.13)	2.01 (0.03)	1.76 (0.12)	1.74 (0.01)	1.45 (0.03)	1.36 (0.33)	1.85 (0.40)	1.71 (0.06)
	$S_5 \leftarrow S_0$	1.95 (0.13)	1.87 (0.01)	2.04 (0.04)	2.08 (0.01)	1.88 (0.02)	1.78 (0.41)	1.64 (0.01)	1.50 (0.02)	1.89 (0.10)	1.93 (0.24)
7	$S_1 \leftarrow S_0$	1.09 (0.01)	1.13 (0.11)	1.21 (0.40)	1.17 (0.32)	1.18 (0.16)	1.23 (0.04)	0.52 (0.02)	0.50 (0.01)	1.01 (0.07)	1.17 (0.07)
	$S_2 \leftarrow S_0$	1.31 (0.09)	1.44 (0.09)	1.79 (0.05)	1.41 (0.15)	1.38 (0.08)	1.39 (0.03)	0.72 (0.06)	0.66 (0.13)	1.47 (0.06)	1.19 (0.05)
	$S_3 \leftarrow S_0$	1.45 (0.09)	1.50 (0.12)	1.85 (0.10)	1.88 (0.11)	1.61 (0.14)	1.52 (0.11)	1.30 (0.11)	1.15 (0.04)	1.64 (0.08)	1.54 (0.03)
	$S_4 \leftarrow S_0$	1.71 (0.01)	1.65 (0.01)	1.99 (0.05)	1.96 (0.01)	1.64 (0.04)	1.73 (0.31)	1.49 (0.04)	1.37 (0.34)	1.74 (0.49)	1.61 (0.07)
	$S_5 \leftarrow S_0$	1.74 (0.29)	1.82 (0.01)	2.03 (0.01)	2.23 (0.47)	1.87 (0.03)	1.81 (0.07)	1.74 (0.09)	1.55 (0.05)	1.91 (0.11)	1.84 (0.14)
8	$S_1 \leftarrow S_0$	1.46 (0.01)	1,46 (0.08)	1.39 (0.11)	1.33 (0.09)	1.50 (0.13)	1.46 (0.10)	0.46 (0.01)	0.58 (0.04)	1.29 (0.13)	1.29 (0.14)
	$S_2 \leftarrow S_0$	1.53 (0.11)	1.63 (0.01)	1.55 (0.01)	1.74 (0.10)	1.64 (0.01)	1.73 (0.04)	0.81 (0.07)	0.67 (0.01)	1.61 (0.03)	1.51 (0.01)
	$S_3 \leftarrow S_0$	1.89 (0.02)	1.82 (0.05)	1.96 (0.11)	2.07 (0.14)	1.94 (0.11)	1.89 (0.04)	1.51 (0.01)	1.38 (0.06)	1.87 (0.11)	1.88 (0.11)
	$S_4 \leftarrow S_0$	1.94 (0.01)	2.03 (0.03)	2.01 (0.07)	2.23 (0.15)	2.06 (0.06)	2.00 (0.07)	1.79 (0.05)	1.59 (0.01)	2.22 (0.03)	2.18 (0.01)
	$S_5 \leftarrow S_0$	2.16 (0.14)	2.17 (0.15)	2.30 (0.04)	2.56 (0.20)	2.10 (0.03)	2.10 (0.06)	1.80 (0.10)	1.96 (0.19)	2.37 (0.21)	2.34 (0.03)
9	$S_1 \leftarrow S_0$	1.54 (0.16)	1.51 (0.14)	1.28 (0.15)	1.27 (0.15)	1.53 (0.18)	*=1-3*	0.58 (0.01)	*=1-8*	*=1-5*	*=1-4*
	$S_2 \leftarrow S_0$	1.92 (0.03)	1.80 (0.05)	1.81 (0.01)	1.70 (0.06)	1.72 (0.01)	*=1-3*	0.60 (0.04)	*=1-8*	*=1-5*	*=1-4*
	$S_3 \leftarrow S_0$	2.06 (0.07)	2.00 (0.11)	1.85 (0.07)	1.88 (0.06)	1.98 (0.14)	*=1-3*	1.32 (0.06)	*=1-8*	*=1-5*	*=1-4*
	$S_4 \leftarrow S_0$	2.30 (0.08)	2.09 (0.03)	1.99 (0.06)	1.96 (0.05)	2.04 (0.04)	*=1-3*	1.75 (0.12)	*=1-8*	*=1-5*	*=1-4*
	$S_5 \leftarrow S_0$	2.38 (0.23)	2.32 (0.03)	2.20 (0.01)	2.37 (0.26)	2.30 (0.01)	*=1-3*	1.94 (0.06)	*=1-8*	*=1-5*	*=1-4*
10	$S_1 \leftarrow S_0$	1.24 (0.02)	1.16 (0.04)	1.52 (0.01)	1.48 (0.07)	1.38 (0.05)	1.36 (0.03)	0.46 (0.01)	0.72 (0.01)	1.14 (0.06)	1.15 (0.04)
	$S_2 \leftarrow S_0$	1.50 (0.06)	1.50 (0.01)	1.60 (0.17)	1.64 (0.13)	1.50 (0.04)	1.65 (0.03)	0.69 (0.03)	0.83 (0.08)	1.53 (0.06)	1.23 (0.03)
	$S_3 \leftarrow S_0$	1.69 (0.01)	1.62 (0.04)	2.27 (0.17)	2.22 (0.23)	1.85 (0.02)	1.77 (0.02)	1.71 (0.02)	1.40 (0.02)	1.79 (0.09)	1.75 (0.12)
	$S_4 \leftarrow S_0$	1.98 (0.18)	1.80 (0.07)	2.27 (0.07)	2.38 (0.10)	1.98 (0.15)	2.03 (0.23)	1.74 (0.04)	1.97 (0.22)	2.20 (0.22)	2.27 (0.17)
	$S_5 \leftarrow S_0$	2.11 (0.02)	2.16 (0.18)	2.36 (0.11)	2.42 (0.17)	2.17 (0.15)	2.27 (0.07)	1.85 (0.03)	2.11 (0.25)	2.49 (0.02)	2.31 (0.10)
11	$S_1 \leftarrow S_0$	1.41 (0.03)	1.19 (0.02)	1.81 (0.18)	1.71 (0.14)	1.54 (0.07)	1.58 (0.08)	0.40 (0.01)	0.62 (0.05)	1.21 (0.07)	1.21 (0.07)
	$S_2 \leftarrow S_0$	1.66 (0.03)	1.77 (0.11)	2.37 (0.10)	1.88 (0.08)	1.72 (0.02)	1.81 (0.01)	0.76 (0.03)	0.80 (0.01)	1.63 (0.02)	1.34 (0.01)
	$S_3 \leftarrow S_0$	1.87 (0.05)	1.83 (0.04)	2.44 (0.35)	2.39 (0.32)	2.01 (0.08)	2.00 (0.07)	1.83 (0.01)	1.41 (0.04)	1.85 (0.18)	1.63 (0.01)
	$S_4 \leftarrow S_0$	2.02 (0.01)	2.24 (0.02)	2.48 (0.04)	2.49 (0.13)	2.13 (0.19)	2.19 (0.21)	1.97 (0.10)	2.03 (0.01)	2.44 (0.26)	1.86 (0.17)
	$S_5 \leftarrow S_0$	2.11 (0.20)	2.30 (0.10)	2.51 (0.13)	2.51 (0.10)	2.36 (0.01)	2.17 (0.03)	2.28 (0.31)	2.06 (0.21)	2.74 (0.01)	2.46 (0.26)

Table S-4 First five dipole-allowed lowest-lying (singlet) vertical excitation energies (in eV) and corresponding oscillator strength values (in parentheses), for all tautomers of the neutral ACP derivatives. Only excitations with oscillator strengths ≥ 0.01 have been considered. All values have been obtained with the B3LYP functional.

S4 Impact of Solvation on the Absorption Spectra

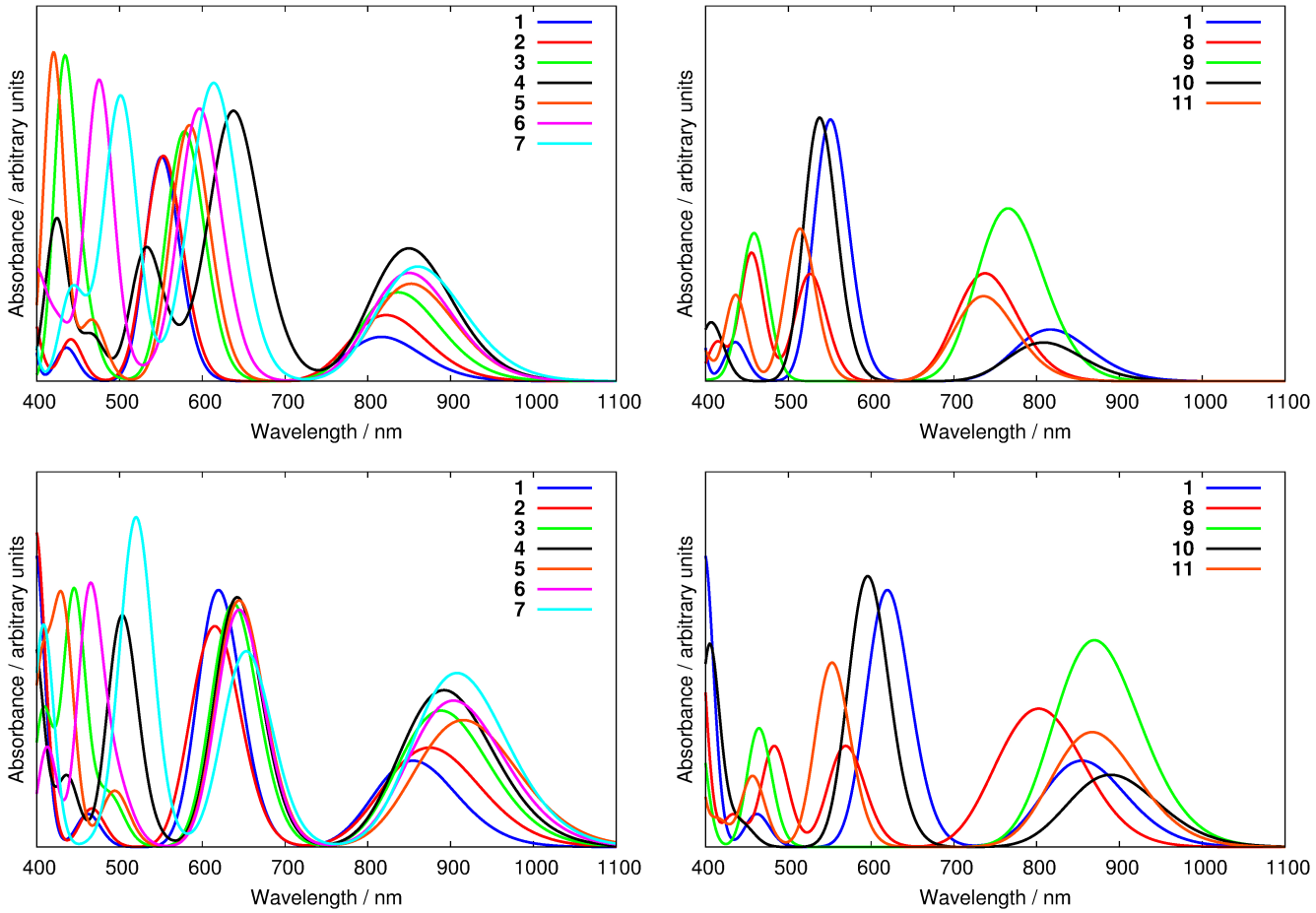


Fig. S-2 Absorption spectra of the diprotonated dicationic forms of the azacalixphyrins studied in this work, in gas phase (top) and in DMSO solution (bottom). All curves have been obtained with the CAM-B3LYP functional.

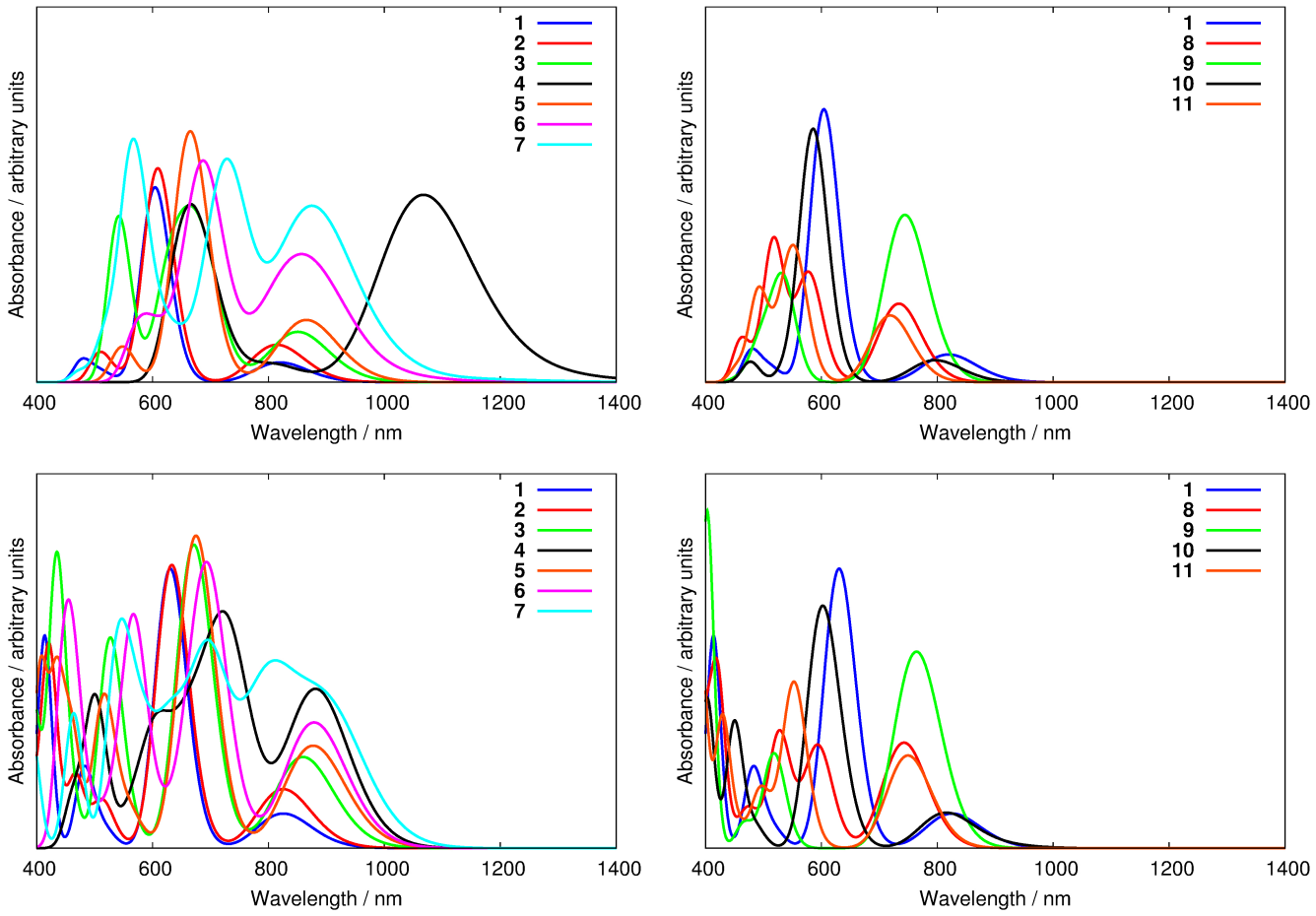


Fig. S-3 Absorption spectra of the diprotonated dicationic forms of the azacalixphyrins studied in this work, in gas phase (top) and in DMSO solution (bottom). All curves have been obtained with the B3LYP functional.

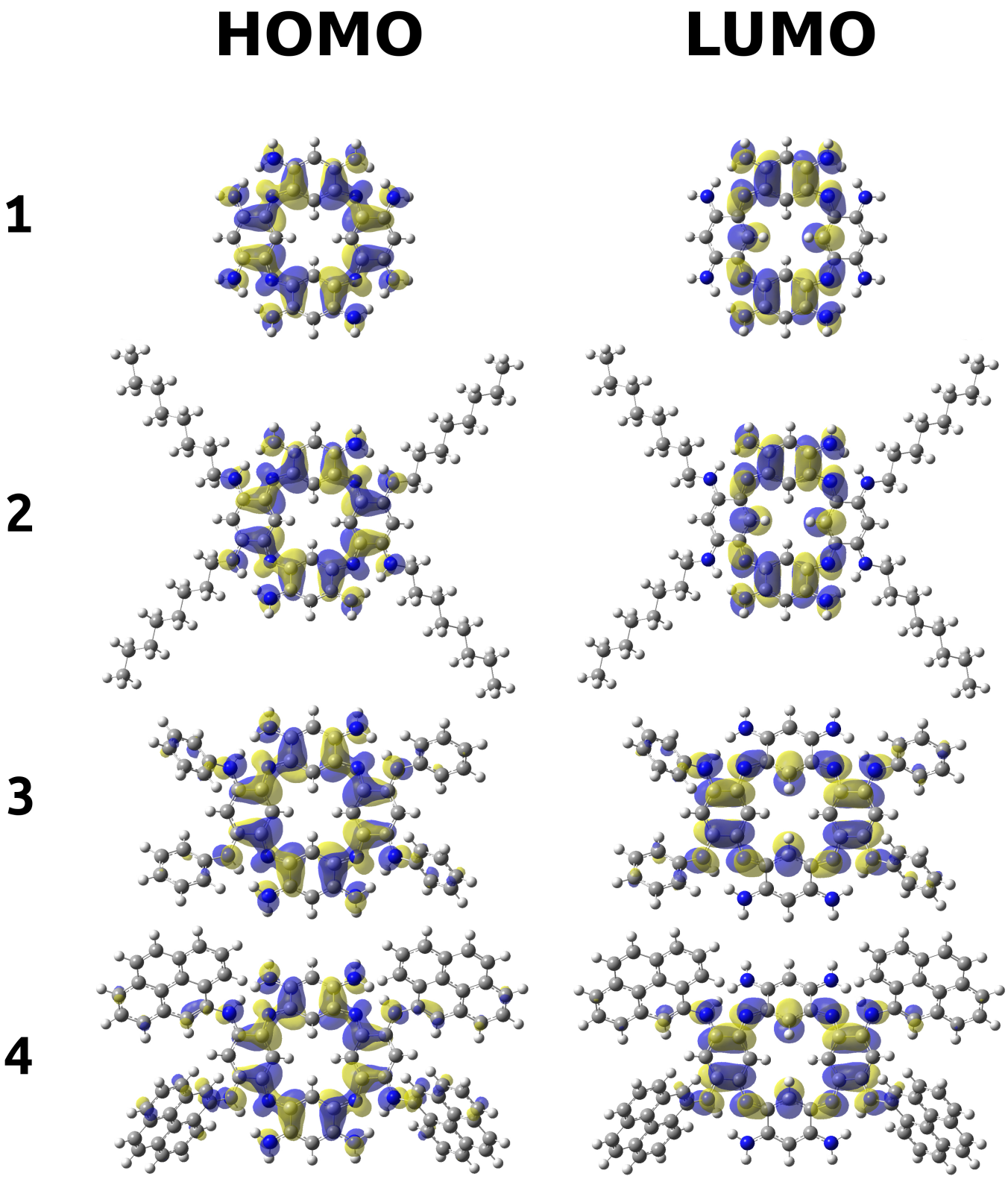


Fig. S-4 CAM-B3LYP HOMO and LUMO of the diprotonated dicationic forms of the ACPs **1**–**4**.

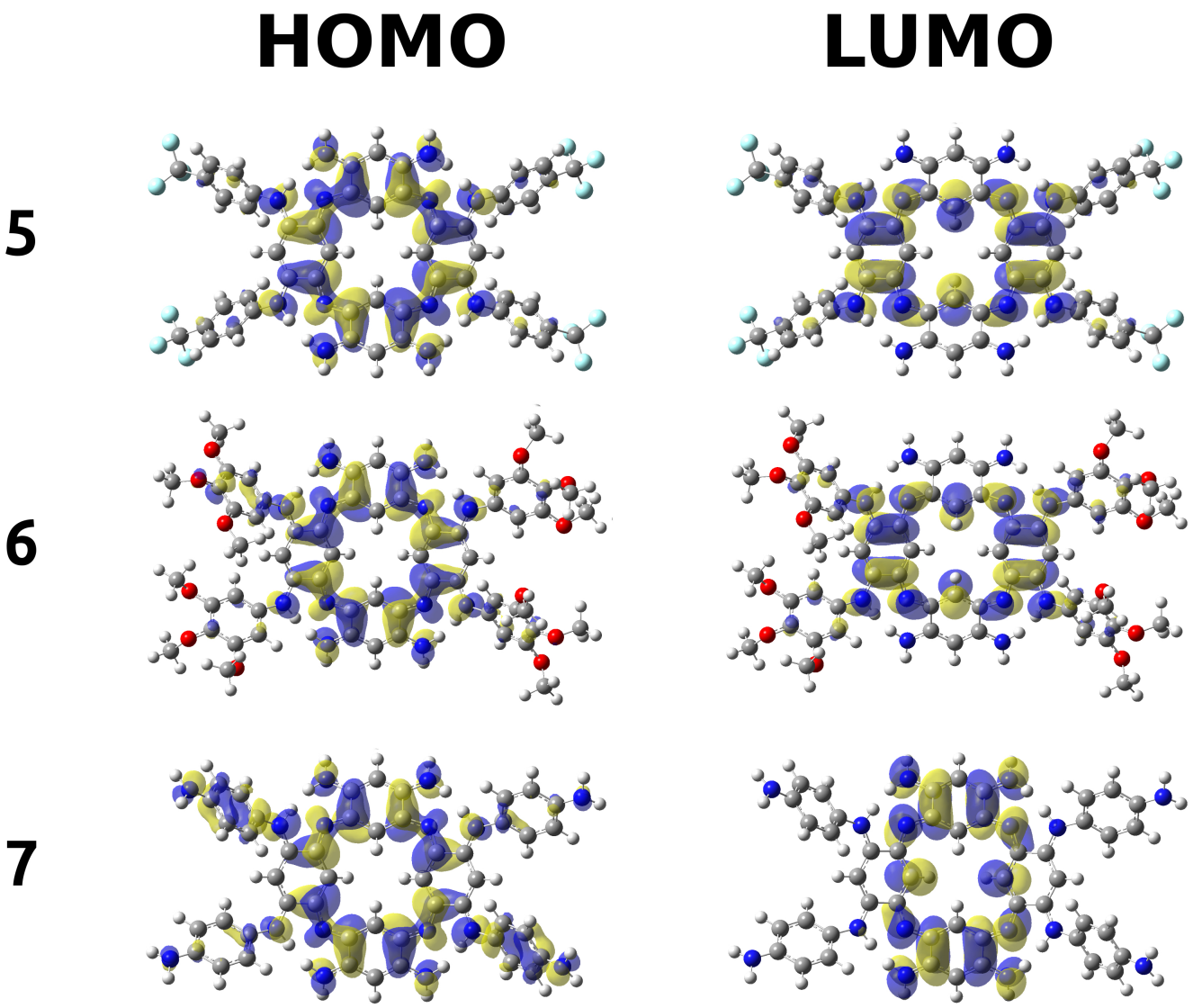


Fig. S-5 CAM-B3LYP HOMO and LUMO of the diprotonated dicationic forms of the ACPs 5–7.

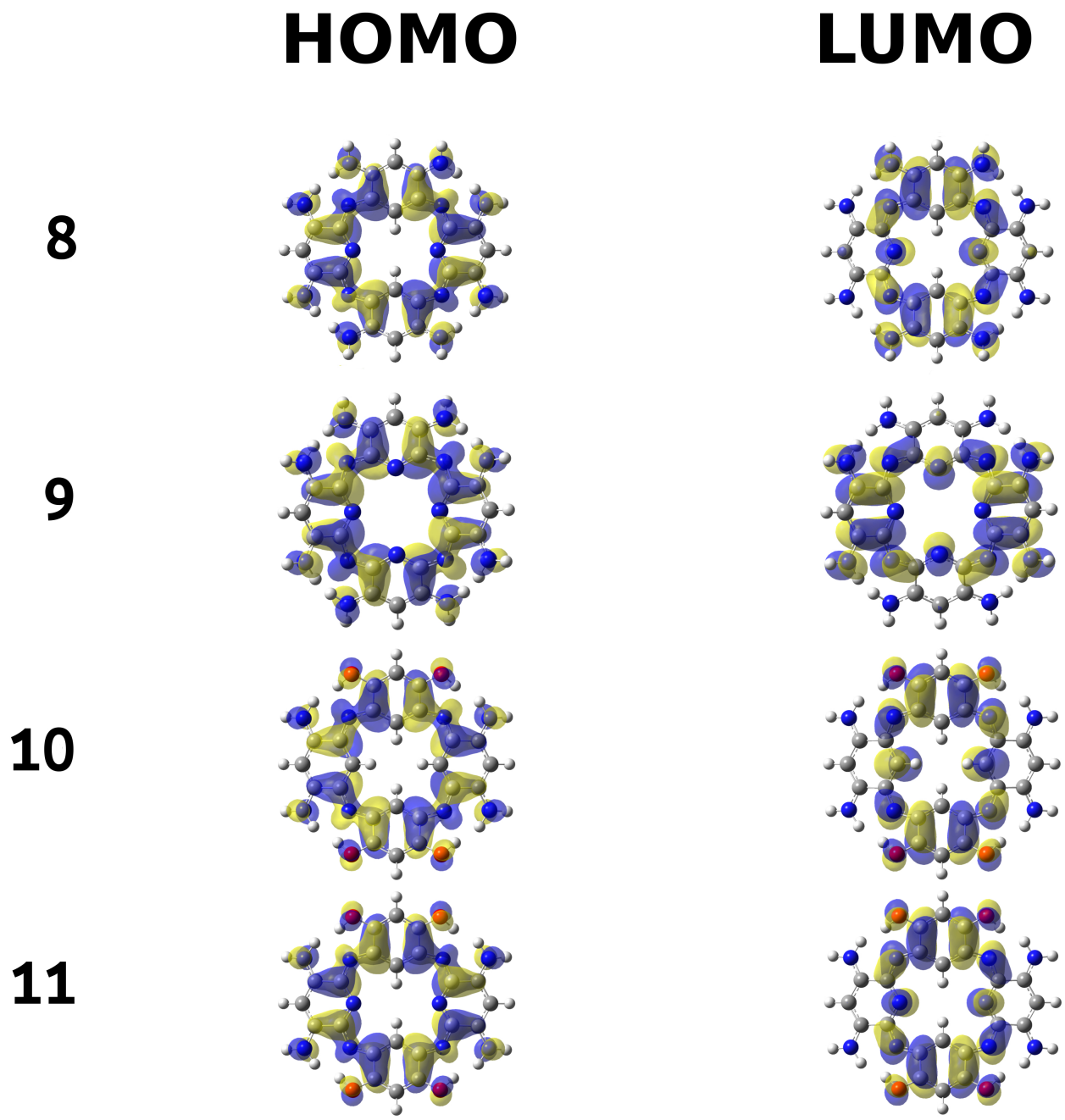


Fig. S-6 CAM-B3LYP HOMO and LUMO of the diprotonated dicationic forms of the ACPSs **8**–**11**.

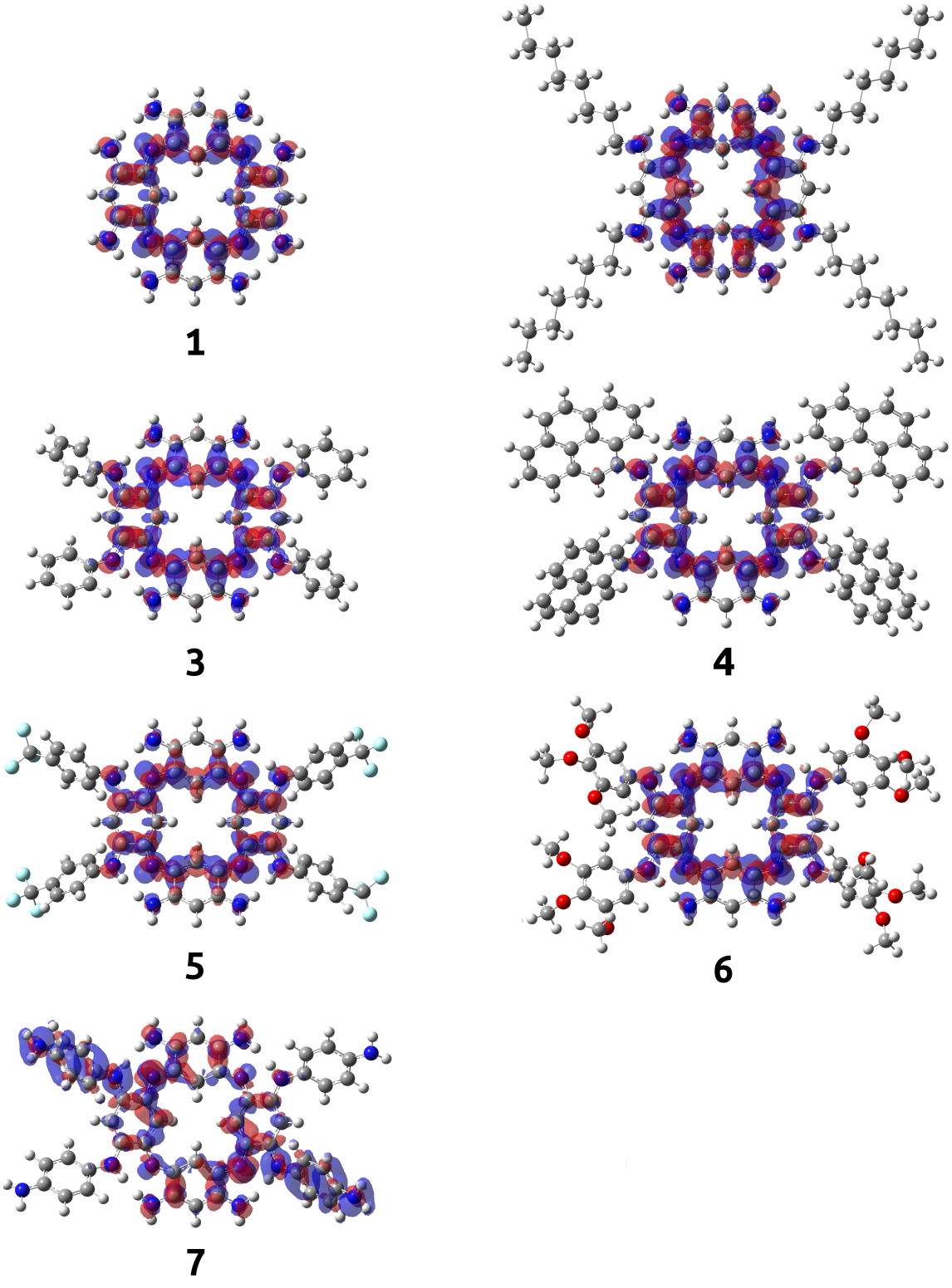


Fig. S-7 Density difference plot corresponding to the transition to the lowest excited-states in ACPs **1**–7 in their diprotonated dicationic forms. Red (blue) regions indicate an increase (decrease) of electron density upon absorption of light. All densities have been obtained with the CAM-B3LYP functional.

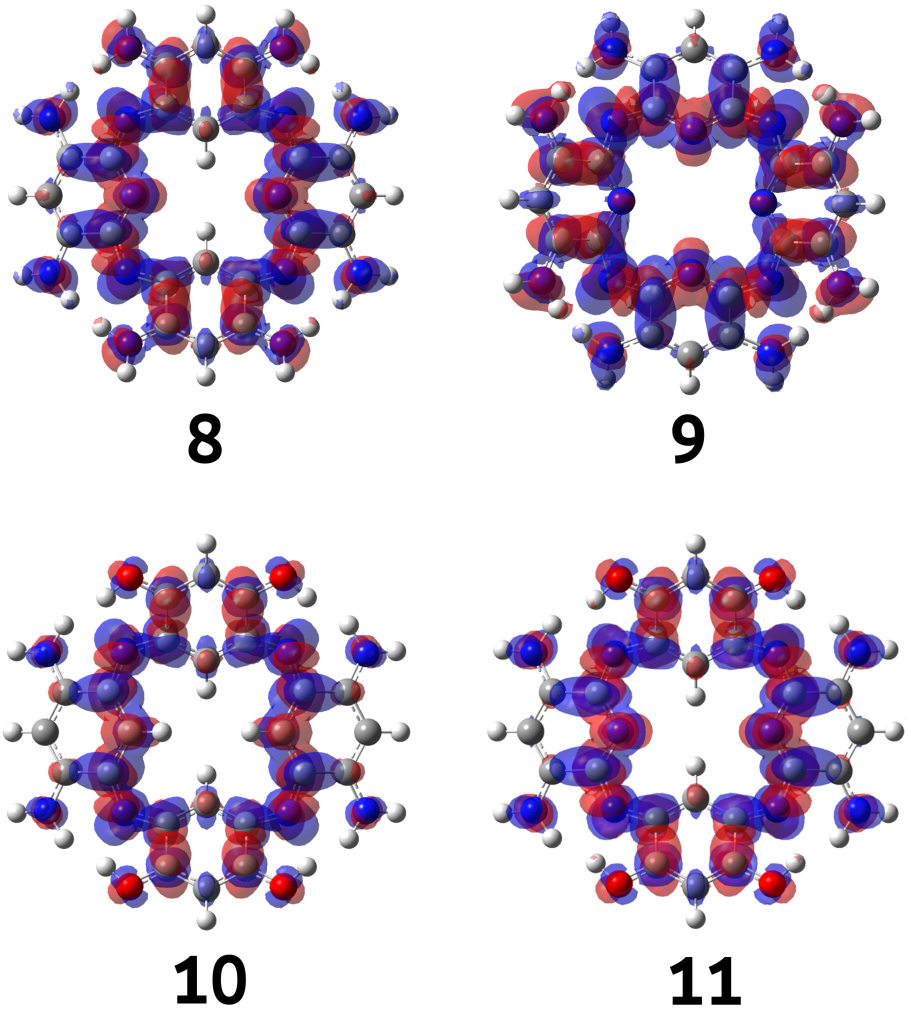


Fig. S-8 Density difference plot corresponding to the transition to the lowest excited-states in ACPs **8**–**11** in their diprotonated dicationic forms. See caption of Figure S-7 for more details.

S5 Molecular Geometries

S5.1 $2H^+$ Forms

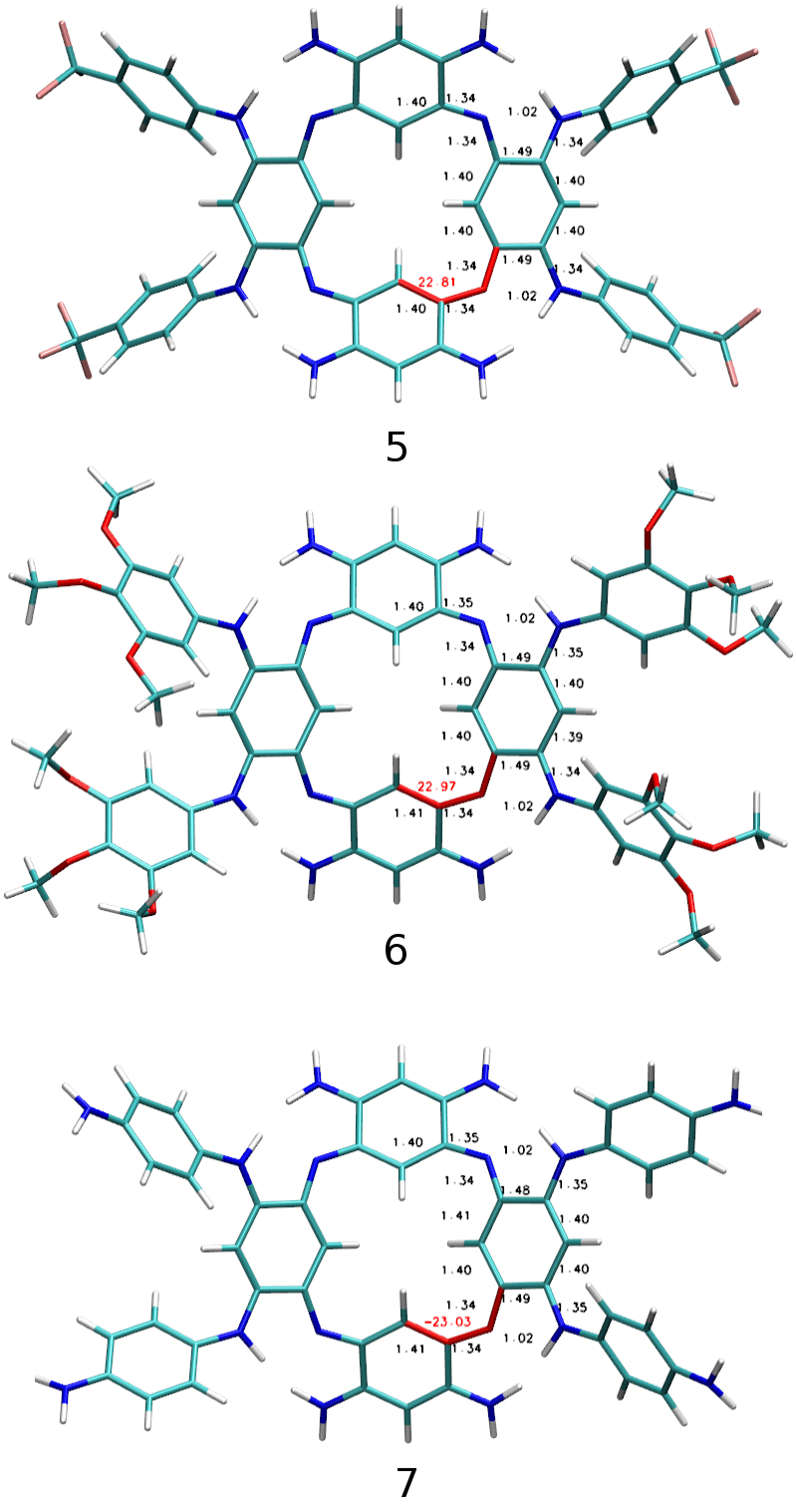
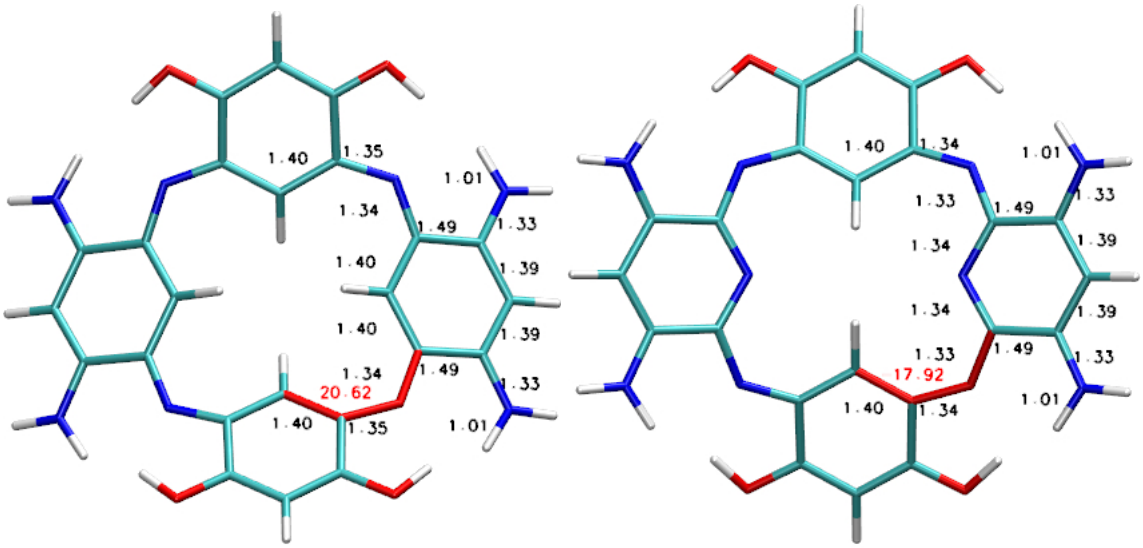


Fig. S-9 Bond lengths (in Å) and dihedral angle (in °) formed by the four atoms in red, denoted ϕ, for the dicationic diprotonated forms of ACPs **5**, **6**, and 7.



10 11

Fig. S-10 Geometries of **10** and **11**, see caption of Figure S-9 for more details.

S5.2 Neutral Forms

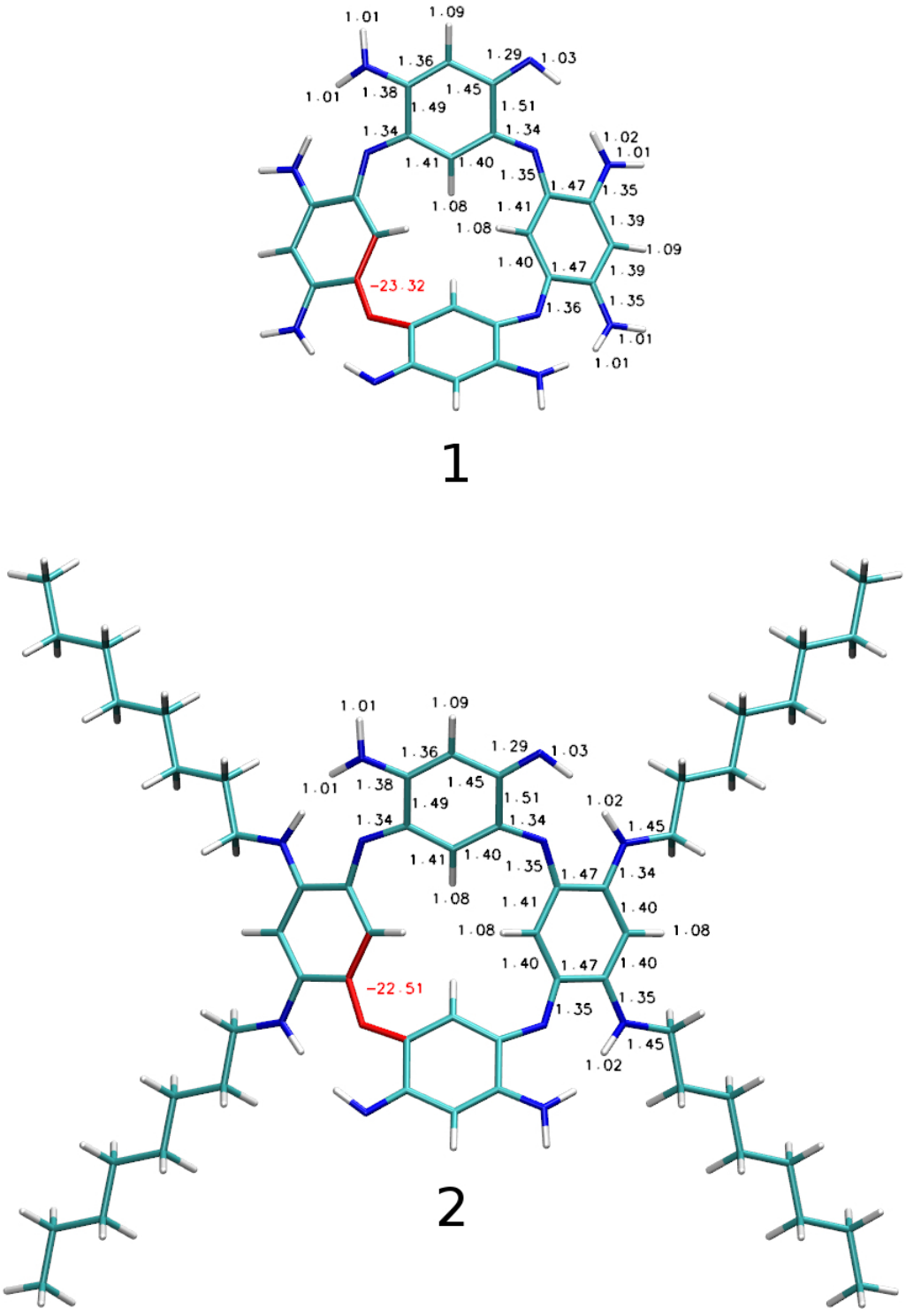
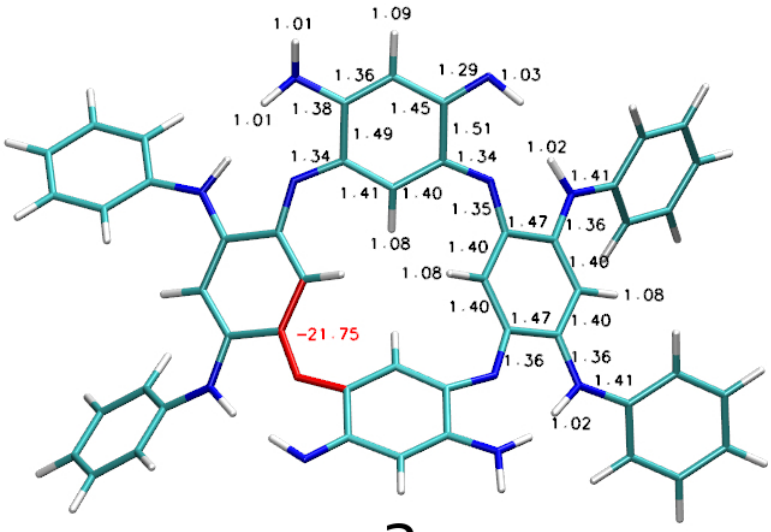
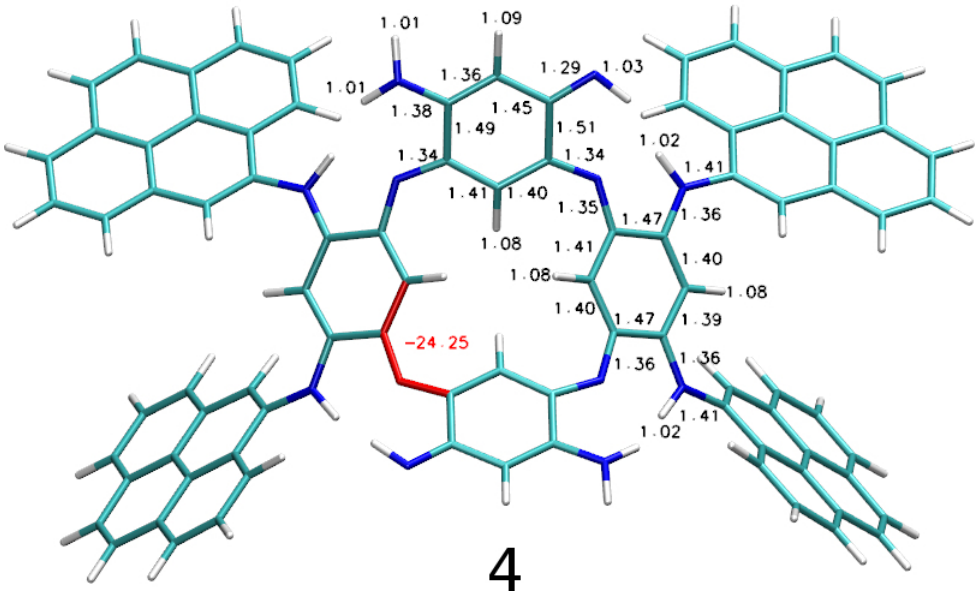


Fig. S-11 Molecular bond lengths (in Å) and dihedral angle (in °) formed by the four atoms in red, denoted ϕ, for the neutral forms of azacalixphyrins **1** and **2** in their 1-5 tautomeric forms.

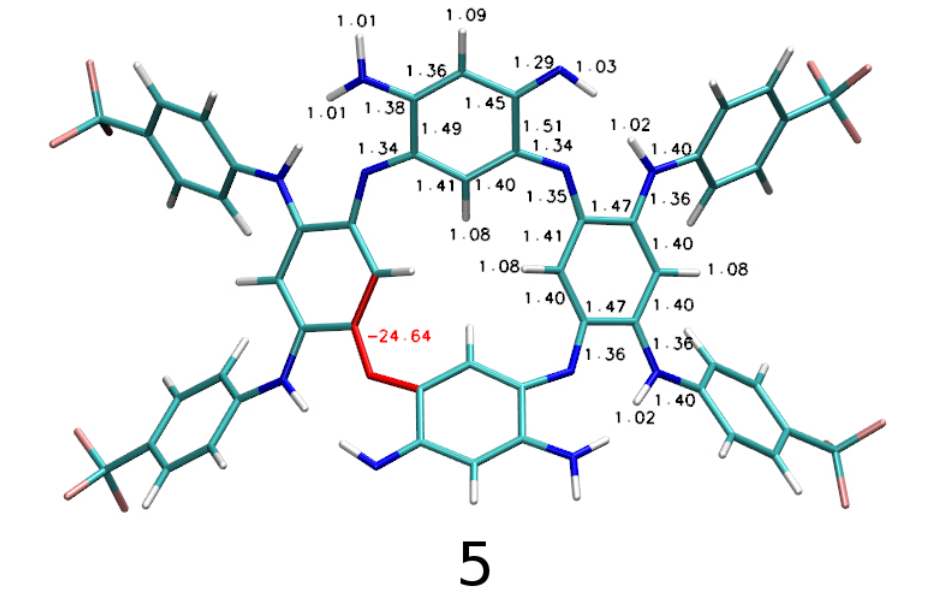


3

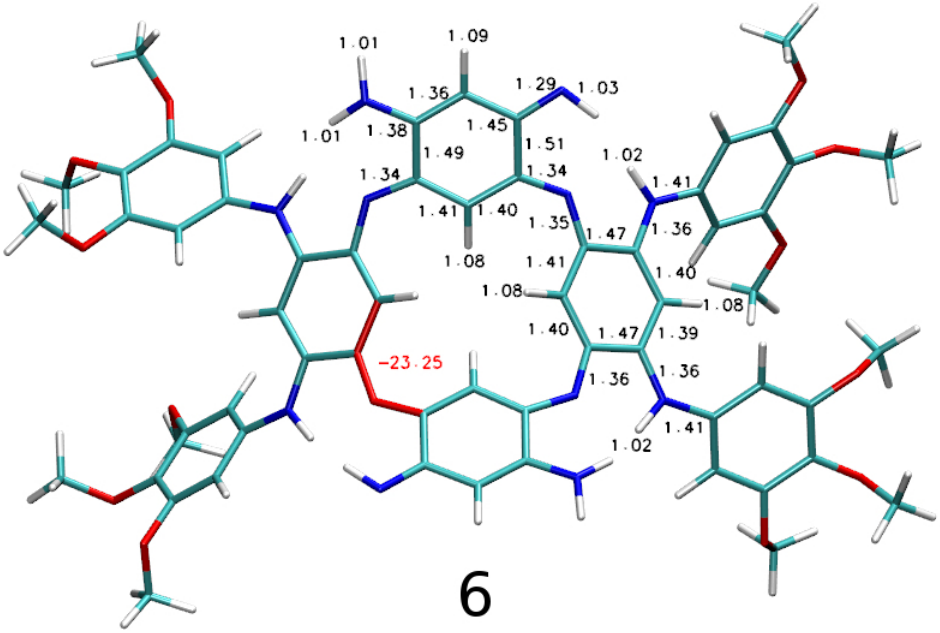


4

Fig. S-12 Molecular structure of ACPs **3** and **4**. See caption of Figure S-11 for more details.



5



6

Fig. S-13 Molecular structure of ACPs **5** and **6**. See caption of Figure S-11 for more details.

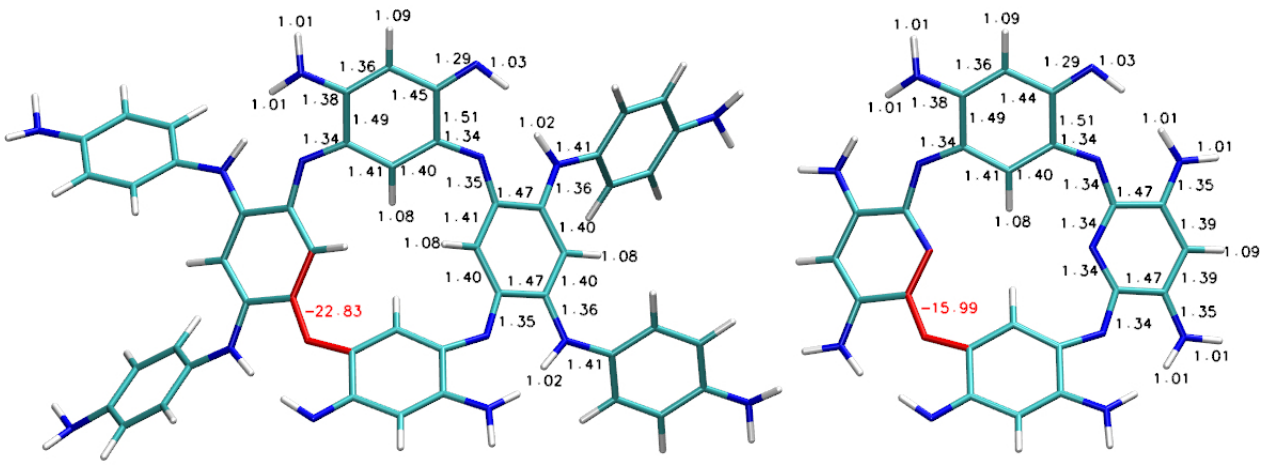


Fig. S-14 Molecular structure of ACPs **7** and **8**. See caption of Figure S-11 for more details.

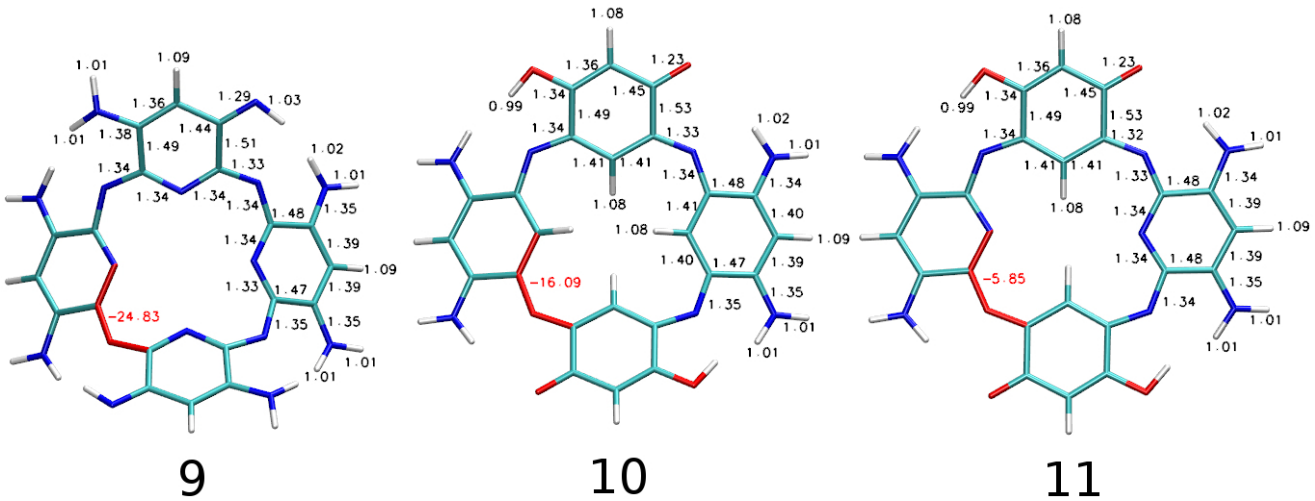


Fig. S-15 Molecular structure of ACPs **9**, **10** and **11**. See caption of Figure S-11 for more details.