Supplementary Information

Shape-responsive host-guest chemistry: metal-free tetra cationic porphyrin nonplanarity promoted by clay mineral interactions assessed by theoretical simulations

Eduardo Diaz Suarez,[a] Filipe Camargo Dalmatti Alves Lima,[b] Arles V. Gil Rebaza,[c,d] Vera Regina Leopoldo Constantino,[e*] Helena Maria Petrilli [a*]

[a] Departamento de Física dos Materiais e Mecânica, Instituto de Física, Universidade de São Paulo, C. P. 66318, São Paulo, SP, 05508-090, Brazil, *e-mail: hmpetril@if.usp.br

[b] Instituto Federal de Educação Ciência e Tecnologia de São Paulo, Campus Matão, SP, 15991-502, Brazil

[c] Instituto de Física La Plata IFLP, CCT La Plata – CONICET, 1900 La Plata, Argentina

[d] Departamento de Física, Fac. de Ciencias Exactas de la Universidad Nacional de La Plata UNLP, 1900 La Plata, Argentina

[e] Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes 748, São Paulo, SP, 05508-000, Brazil *e-mail: vrlconst@iq.usp.br

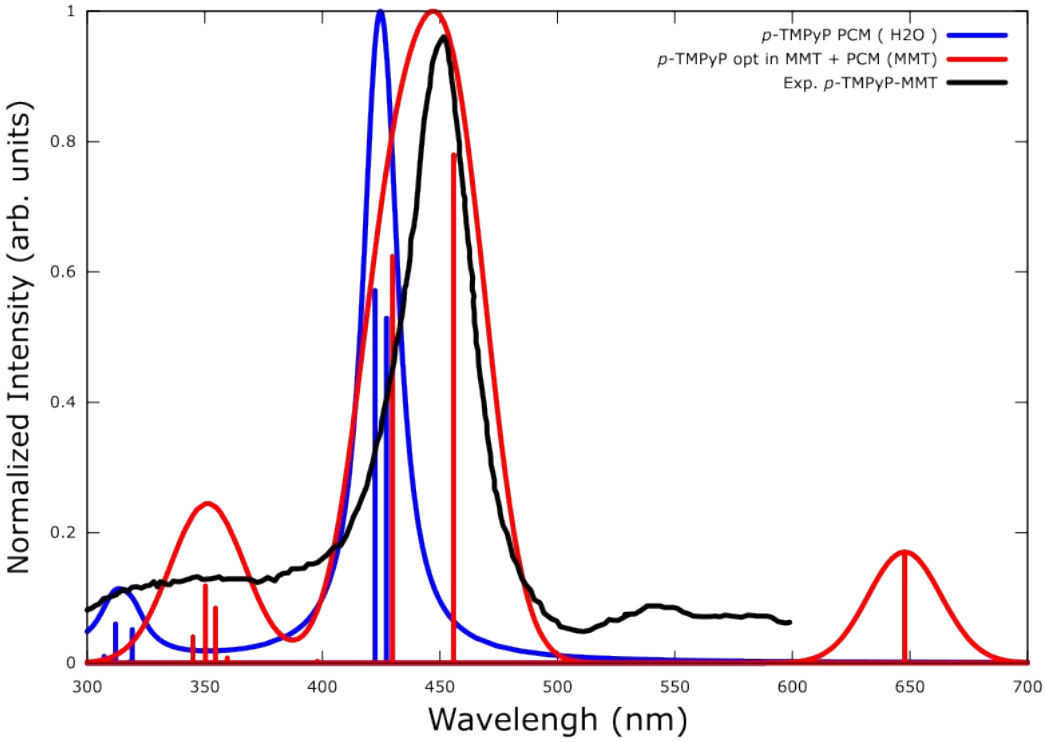

Fig. S1 Simulated UV-Vis electronic spectra of *p*-TMPyP under different conditions. The blue line represents the single molecule using water dielectric constant values. The red line represents the *p*-TMPyP single molecule that was geometrically optimised on the MMT surface and extracted for the UV-Vis simulation; the values employed by the PCM dielectric constant mimicked the MMT environment. The black line shows the experimental UV-Vis electronic spectrum of the TMPyP-MMT (M. O. Senge, *ECS Trans*, 2015, **66**, 1–10).

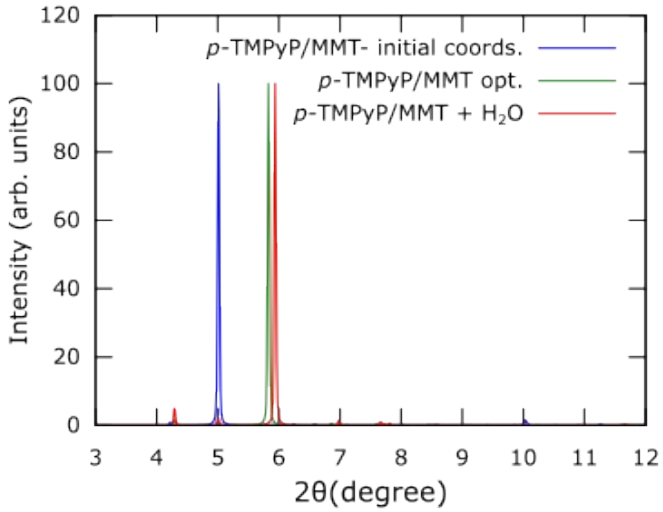

Fig. S2 Simulated X-ray diffraction pattern of *p*-TMPyP intercalated into MMT without structural optimisation (blue line), after structural optimisation in an anhydrous environment (green line), and after structural optimisation with water molecules randomly located between the layers (red line).

Table S1 Average bond lengths between atoms in simulated Na-MMT structure.

	Bond length (Å)
Si-O (basal)	1.6489
Si-O (apical)	1.8250
Al-O	1.9142
Mg-O	2.0728
O-H	0.9753

Table S2 Optimised bond lengths (Å) in *p*-TMPyP in a vacuum and adsorbed on (001) MMT surface.

Bonds	**Bond length of *p*-TMPyP-vacuum**	**Bond length of *p*-TMPyP-MMT**
Pyrrol1 C_α-C_β	1.47	1.45
Pyrrol2 C_α-C_β	1.44	1.42
Pyrrol3 C_α-C_β	1.47	1.45
Pyrrol4 C_α-C_β	1.44	1.42
(average valour)	1.46	1.44
Pyrrol1 C_α-C_{meso}	1.41	1.43
Pyrrol2 C_α-C_{meso}	1.41	1.43
Pyrrol3 C_α-C_{meso}	1.41	1.43
Pyrrol4 C_α-C_{meso}	1.41	1.43
(average valour)	1.41	1.43
C_β-C_{meso}	2.54	2.53
C_β-C_{meso}	2.55	2.54
C_β-C_{meso}	2.54	2.53
C_β-C_{meso}	2.55	2.54
(average valour)	2.55	2.54
Pyrrol2 H- Pyrrol4 H	2.22	2.42

Table S3. Optimised dihedral angles (°) of *p*-TMPyP in a vacuum and adsorbed on the (001) MMT surface.

Bonds	Dihedral angles of *p*-TMPy-vacuum	Dihedral angles of *p*-TMPyP-MMT
Pyrrol1 C_α-C_{meso}-C_α-C_β Pyrrol2	175.27	163.50
Pyrrol2 C_β-C_α-C_{meso}-C_α Pyrrol3	175.22	163.16
Pyrrol3 C_α-C_{meso}-C_α-C_β Pyrrol4	175.27	165.56
Pyrrol4 C_β-C_α-C_{meso}-C_α Pyrrol1	175.17	165.46
(average valour)	175.23	164.42
Methyl-pyridyl dihedral 1	64.27	44.30
Methyl-pyridyl dihedral 2	64.38	44.92
Methyl-pyridyl dihedral 3	63.78	43.88
Methyl-pyridyl dihedral 4	63.71	43.37
(average valour)	64.04	44.12

Table S4 Optimised bond lengths (Å) of *p*-TMPyP on MMT, *p*-TMPyP intercalated into anhydrous MMT, and *p*-TMPyP intercalated into hydrated MMT.

Bonds	Bond length in *p*-TMPyP on MMT	Bond length in *p*-TMPyP intercalated into anhydrous MMT	Bond length in *p*-TMPyP intercalated into hydrated MMT
Pyrrol1 C_α-C_β	1.44	1.45	1.42
Pyrrol2 C_α-C_β	1.41	1.41	1.42
Pyrrol3 C_α-C_β	1.44	1.45	1.42
Pyrrol4 C_α-C_β	1.41	1.41	1.42
(average valour)	1.43	1.43	1.42
Pyrrol1 C_α-C_{meso}	1.43	1.43	1.45
Pyrrol2 C_α-C_{meso}	1.43	1.44	1.45
Pyrrol3 C_α-C_{meso}	1.43	1.43	1.45
Pyrrol4 C_α-C_{meso}	1.43	1.44	1.44
(average valour)	1.43	1.44	1.45
C_β-C_{meso}	2.53	2.54	2.56
C_β-C_{meso}	2,54	2.54	2.55
C_β-C_{meso}	2.53	2.53	2.55
C_β-C_{meso}	2.54	2.54	2.52
(average valour)	2.54	2.54	2.55

Table S5. Optimised dihedral angles (°) of *p*-TMPyP on MMT, *p*-TMPyP intercalated into anhydrous MMT, and *p*-TMPyP intercalated into hydrated MMT.

Bonds	Dihedral angles of *p*-TMPyP on MMT	Dihedral angles of *p*-TMPyP intercalated into anhydrous MMT	Dihedral angles of *p*-TMPyP intercalated into hydrated MMT
Pyrrol1 C_α-C_{meso}-C_α-C_β Pyrrol2	159.63	159.43	150.68
Pyrrol2 C_β-C_α-C_{meso}-C_α Pyrrol3	159.85	160.53	160.58
Pyrrol3 C_α-C_{meso}-C_α-C_β Pyrrol4	161.60	158.11	144.89
Pyrrol4 C_β-C_α-C_{meso}-C_α Pyrrol1	161.94	159.12	149.35
(average valour)	161.38	159.30	151.38
Methyl-pyridyl dihedral 1	43.39	41.12	34.97
Methyl-pyridyl dihedral 2	43.53	41.94	39.49
Methyl-pyridyl dihedral 3	42.76	40.11	35.89
Methyl-pyridyl dihedral 4	42.75	39.44	44.15
(average valour)	43.10	40.65	38.63

Table S6 Optimised bond lengths **(Å)** *m*-TMPyP intercalated into anhydrous MMT and *m*-TMPyP intercalated into hydrated MMT.

Bonds	Bond length in *m*-TMPyP intercalated into anhydrous MMT	Bond length in *m*-TMPyP intercalated into hydrated MMT
Pyrrol1 C_α-C_β	1.47	1.43
Pyrrol2 C_α-C_β	1.44	1.43
Pyrrol3 C_α-C_β	1.47	1.44
Pyrrol4 C_α-C_β	1.44	1.43
(average valour)	1.46	1.43
Pyrrol1 C_α-C_{meso}	1.41	1.44
Pyrrol2 C_α-C_{meso}	1.41	1.42
Pyrrol3 C_α-C_{meso}	1.41	1.44
Pyrrol4 C_α-C_{meso}	1.41	1.42
(average valour)	1.41	1.43
C_β-C_{meso}	2.54	2.52
C_β-C_{meso}	2.55	2.55
C_β-C_{meso}	2.54	2.54
C_β-C_{meso}	2.55	2.55
(average valour)	2.55	2.54

Table S7 Optimised dihedral angles (°) of *m*-TMPyP intercalated into anhydrous MMT and *m*-TMPyP intercalated into hydrated MMT.

Bonds	Dihedral angles of *m*-TMPyP intercalated into anhydrous MMT	Dihedral angles of in *m*-TMPyP intercalated into hydrated MMT
Pyrrol1 C_α-C_{meso}-C_α-C_β Pyrrol2	175.27	171.92
Pyrrol2 C_β-C_α-C_{meso}-C_α Pyrrol3	175.17	170.80
Pyrrol3 C_α-C_{meso}-C_α-C_β Pyrrol4	175.27	163.57
Pyrrol4 C_β-C_α-C_{meso}-C_α Pyrrol1	175.22	156.86
(average valour)	175.23	165.79
Methyl-pyridyl dihedral 1	63.61	51.57
Methyl-pyridyl dihedral 2	63.78	46.05
Methyl-pyridyl dihedral 3	64.27	63.25
Methyl-pyridyl dihedral 4	64.38	60.86
(average valour)	64.01	55.43

Video - The relaxation of the *p*-TMPyP intercalated into MMT

VIDEO-Suarez et al.mp4