Supporting Information

Metal-coordination-driven Mixed Ligand Binding in Supramolecular Bisporphyrin Tweezers

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Instrumentation

Elemental (C, H, and N) analyses were performed on a CE-440 elemental analyzer. ^{1}H NMR spectra were recorded on a JEOL 500 MHz instrument. The residual ^{1}H resonances of the solvents were used as a secondary reference. UV-vis spectra were recorded on a Perkin-Elmer UV-vis spectrometer. ESI-MS spectra were recorded on a waters Micromass Quattro Microtriple quadrapole mass spectrometer.

X-ray Structure Solution and Refinement.

Single-crystal X-ray data were collected at 100 K on a Bruker SMART APEX CCD diffractometer equipped with CRYO Industries low temperature apparatus and intensity data were collected using graphite-monochromated Mo Kα radiation (λ= 0.71073 Å). The data integration and reduction were processed with SAINT software.[1] An absorption correction was applied.[2] The structure was solved by the direct method using SHELXS-97 and was refined on F2 by full-matrix least-squares technique using the SHELXL-2014 program package.[3] Non-hydrogen atoms were refined anisotropically. The protons of the diol guest substrate were directly located in the difference Fourier maps. The other hydrogen atoms were included in calculated positions. In the refinement, hydrogens were treated as riding atoms using SHELXL default parameters.

Experimental:

Materials:

Free base diethylpyrrole bridged bisporphyrin has been synthesized following the reported procedure.[4] Reagents and solvents are purchased from commercial sources and purified by standard procedures before use. Pyrazine, 1,4-dioxane and 2-aminopyrimidine ligands have been purchased from Sigma-Aldrich.

Synthesis of 1

50 mg (0.041 mmol) of the free base bisporphyrin was taken in 20 mL of anhydrous dichloromethane. 250 μL of anhydrous triethylamine followed by $MgBr_2.OEt_2$ (212 mg, 0.82 mmol) were added to it, and stirred under N_2 atmosphere at room temperature for 1 hour. 50 mL of anhydrous dichloromethane was added to the reaction mixture and washed with distilled water once. The solvent was dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. Column chromatography was done over basic alumina using dry CH_2Cl_2: Acetone(1:1) as eluant. Yield 32 mg (60%). Anal. Calc. (found): C, 78.08 (78.19); H, 8.07 (8.15); N, 9.99 (10.16). ESI-MS: *m/z* 1259.7811 ($[M]^+$). UV-Vis (CH_2Cl_2) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 407 (1.96×10^5), 550 (1.28×10^4), 590 (5.20×10^3). ^1H NMR ($CDCl_3$, 295 K): δ, 9.43 (*s*, 2H, 10-meso-*H*), 9.29 (*s*, 4H, 5,15-meso-*H*), 6.66 (*s*, 1H, -N*H*), 6.03 (*s*, 4H, 37-CH_2), 4.00-3.15 (*m*, 32H, -C$H_2$$CH_3$), 1.95-1.30 (*m*, 48H, -CH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 295 K): δ, 16.5, 17.2, 18.6, 19.1,19.8, 20.4, 21.7, 22.5, 23.9, 30.8, 95.3, 96.7, 97.4, 114.7, 115.3, 119.2, 129.6, 138.6, 140.1, 141.3, 141.9, 142.5, 143.2, 143.7, 144.4, 145.7, 146.3, 147.5, 148.8, 149.2, 149.8 ppm.

Synthesis of 1•PYMD

Compound **1** (50 mg, 0.039 mmol) was dissolved in CH_2Cl_2 (5 mL). 2-aminopyrimidine (5.0 mg, 0.05 mmol) was added to it and stirred for about 30 min. The solution obtained was then filtered off to remove any solid residue and carefully layered with acetonitrile at room temperature. On standing for 6-7 days, reddish solid precipitated out which was then isolated by filtration, washed well with n-hexane, and dried well in vacuum. Yield 42 mg (76%). ESI-MS: *m/z* 1356.8589 [**1**•PYMD + 2H]$^+$. UV-vis (CH_2Cl_2) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 409 (1.80×10^5),

426^{sh} (5.00 × 10^4), 551 (1.28 × 10^4), 591 (5.05 × 10^3). ^{1}H NMR ($CDCl_3$, 295 K): δ, 9.52 (*s*, 4H, 5,15-meso-*H*), 9.45 (*s*, 2H, 10-meso-*H*), 7.42 (s, 1H, -N*H*), 6.06 (*s*, 4H, 37-CH_2), 4.18-3.15 (*m*, 32H, -CH_2CH$_3$), 1.90-1.25 (*m*, 48H, -CH$_2$CH_3), -0.20 (*br*, 2H, -C*H*, PYMD), -2.70 (*br*, 1H, -C*H*, PYMD), -3.80 (*br*, 2H, -NH_2, PYMD) ppm. ^{13}C NMR ($CDCl_3$, 295 K): δ, 15.2, 16.4, 18.2, 19.1,19.5, 20.1, 20.9, 21.3, 22.6, 30.4, 93.5, 94.1, 95.5, 96.7, 108.6 (1C, PYMD), 113.4, 116.2, 119.7, 130.4, 137.9, 139.4, 140.7, 141.3, 142.1, 142.8, 143.1, 143.2, 144.5, 145.6, 147.9, 148.4, 149.1, 149.7, 154.3 (2C, PYMD), 157.2 (1C, PYMD) ppm.

Synthesis of 1•$(PYR)_2$

Compound **1** (50 mg, 0.039 mmol) was dissolved in CH_2Cl_2 (5 mL). Pyrazine (9.0 mg, 0.11 mmol) was added to it and stirred for about 30 min. The solution obtained was then filtered off to remove any solid residue and carefully layered with acetonitrile at room temperature. On standing for 6-7 days, reddish solid precipitated out which was then isolated by filtration, washed well with n-hexane, and dried well in vacuum. Yield 37 mg (67%). UV-vis (CH_2Cl_2) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 410 (1.36 × 10^5), 552 (1.25 × 10^4), 592 (5.00 × 10^3). ^{1}H NMR ($CDCl_3$, 295 K): δ, 9.42 (*s*, 4H, 5,15-meso-*H*), 9.35 (*s*, 2H, 10-meso-*H*), 6.75 (*br*, 8H, -C*H,* PYR), 6.70 (s, 1H, -N*H*), 6.06 (*s*, 4H, 37-CH_2), 3.95-3.00 (*m*, 32H, -CH_2CH$_3$), 1.90-1.40 (*m*, 48H, -CH$_2$CH_3) ppm.

Synthesis of 1•$(DXN)_2$

Compound **1** (50 mg, 0.039 mmol) was dissolved in CH_2Cl_2 (5 mL). 1,4-dioxane (10.0 mg, 0.11 mmol) was added to it and stirred for about 30 min. The solution obtained was then filtered off to remove any solid residue and carefully layered with acetonitrile at room temperature. On standing for 6-7 days, reddish solid precipitated out which was then isolated by filtration, washed well with n-hexane, and dried well in vacuum. Yield 39 mg (70%). UV-vis (CH_2Cl_2) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 408 (1.84 × 10^5), 550 (1.24 × 10^4), 590 (5.27 × 10^3). ^{1}H NMR ($CDCl_3$, 295 K): δ, 9.41 (*s*, 4H, 5,15-meso-*H*), 9.35 (*s*, 2H, 10-meso-*H*), 6.68 (s, 1H, -N*H*), 6.10 (*s*, 4H, 37-CH_2), 3.90-3.15 (*m*, 32H, -CH_2CH$_3$), 2.20-2.60 (*br*, 16H, -CH_2, DXN), 1.90-1.40 (*m*, 48H, -CH$_2$CH_3) ppm.

Synthesis of 1•PYMD•PYR

Compound **1** (50 mg, 0.039 mmol) was dissolved in CH_2Cl_2 (5 mL). 2-aminopyrimidine (5.0 mg, 0.06 mmol) was added to it and stirred for about 5 min followed by addition of pyrazine (4.5 mg, 0.05 mmol) and the mixture is stirred for another 15 min. The solution obtained was then filtered off to remove any solid residue and carefully layered with acetonitrile at room temperature. On standing for 6-7 days, reddish solid precipitated out which was then isolated by filtration, washed well with n-hexane, and dried well in vacuum. Yield 42 mg (75%). UV-vis (CH_2Cl_2) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 410 (1.56×10^5), 551 (1.18×10^4), 591 (4.20×10^3). ^{1}H NMR ($CDCl_3$, 295 K): δ, 9.52 (*s*, 4H, 5,15-meso-*H*), 9.44 (*s*, 2H, 10-meso-*H*), 8.30 (s, 4H, C-*H*, PYR), 7.42 (s, 1H, -N*H*), 6.06 (*s*, 4H, 37-CH_2), 4.20-3.15 (*m*, 32H, -C$H_2$$CH_3$), 1.90-1.25 (*m*, 48H, -CH_2CH_3), -0.20 (*br*, 2H, -C*H*, PYMD), -2.80 (*br*, 1H, -C*H*, PYMD), -3.86 (*br*, 2H, -NH_2, PYMD) ppm.

Synthesis of 1•PYMD•DXN

Compound **1** (50 mg, 0.039 mmol) was dissolved in CH_2Cl_2 (5 mL). 2-aminopyrimidine (5.0 mg, 0.05 mmol) was added to it and stirred for about 5 min followed by addition of 1,4-dioxane (5.0 mg, 0.06 mmol) and the mixture is stirred for another 15 min. The solution obtained was then filtered off to remove any solid residue and carefully layered with acetonitrile at room temperature. On standing for 6-7 days, reddish solid precipitated out which was then isolated by filtration, washed well with n-hexane, and dried well in vacuum. Yield 38 mg (67%). UV-vis (CH_2Cl_2) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 410 (1.75×10^5), 550 (1.06×10^4), 590 (2.21×10^3). ^{1}H NMR ($CDCl_3$, 295 K): δ, 9.51 (*s*, 4H, 5,15-meso-*H*), 9.44 (*s*, 2H, 10-meso-*H*), 7.36 (s, 1H, -N*H*), 6.06 (*s*, 4H, 37-CH_2), 4.20-3.15 (*m*, 32H, -C$H_2$$CH_3$), 3.40 (*br*, 8H, C$H_2$, DXN), 1.90-1.25 (*m*, 48H, -CH_2CH_3), -0.20 (*br*, 2H, -C*H*, PYMD), -2.80 (*br*, 1H, -C*H*, PYMD), -3.86 (*br*, 2H, -NH_2, PYMD) ppm.

References

(1) SAINT+, 6.02 ed., Bruker AXS, Madison, WI, **1999**.

(2) Sheldrick, G.M. SADABS 2.0, **2000**.

(3) Sheldrick, G. M. *SHELXL-2014: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, **2014**.

(4) Yashunsky, D. V.; Arnold, D. P.; Ponomarev, G. V. *Chem. Heterocycl. Comp.* **2000**, *36*, 275.

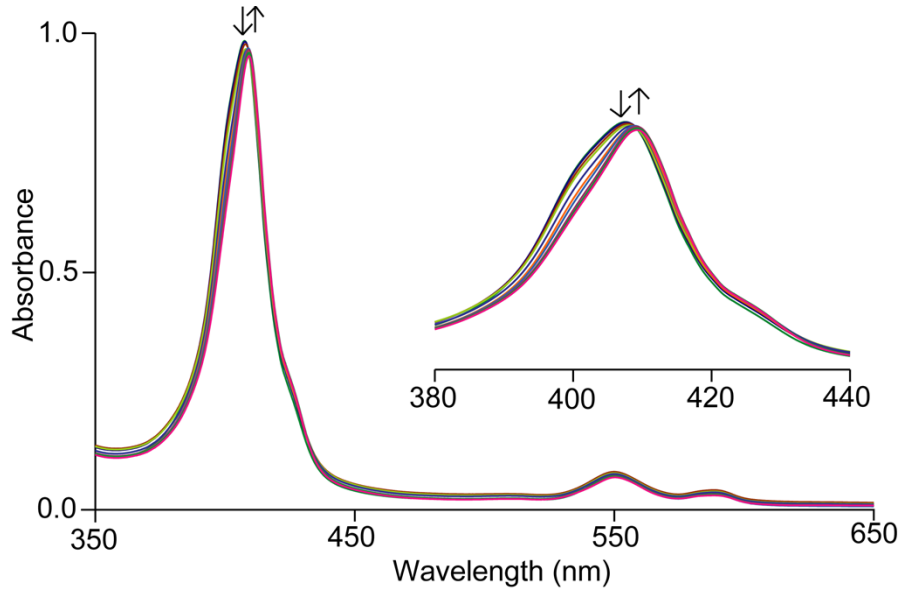

Figure S1. UV-visible spectral changes of **1** (5×10^{-6} M) in dichloromethane upon addition of PYMD as the host: guest molar ratio changes from 1:0.1 to 1:5 at 295 K.

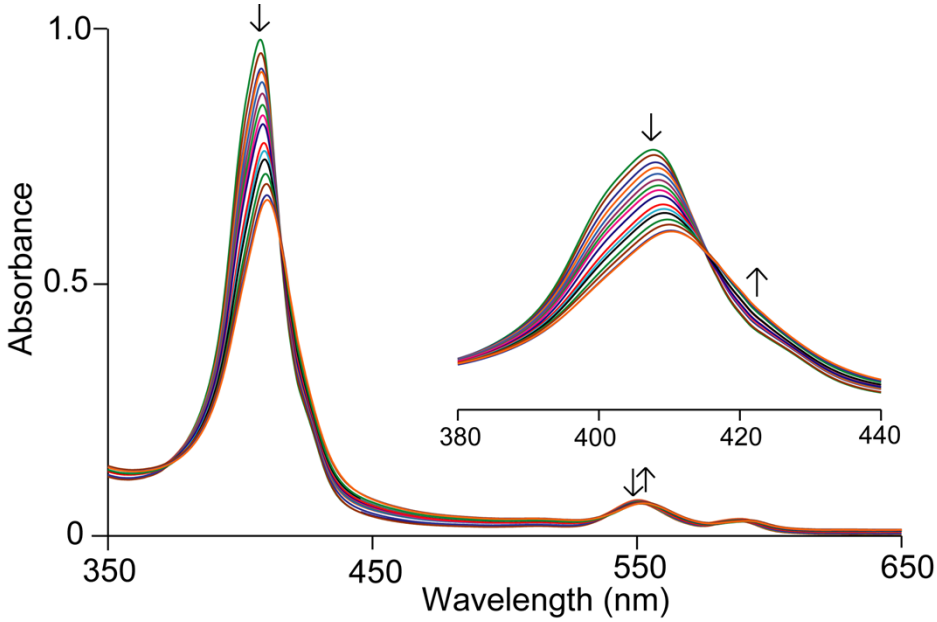

Figure S2. UV-visible spectral changes of **1** (5×10^{-6} M) in dichloromethane upon addition of PYR as the host: guest molar ratio changes from 1:0.1 to 1:944 at 295 K.

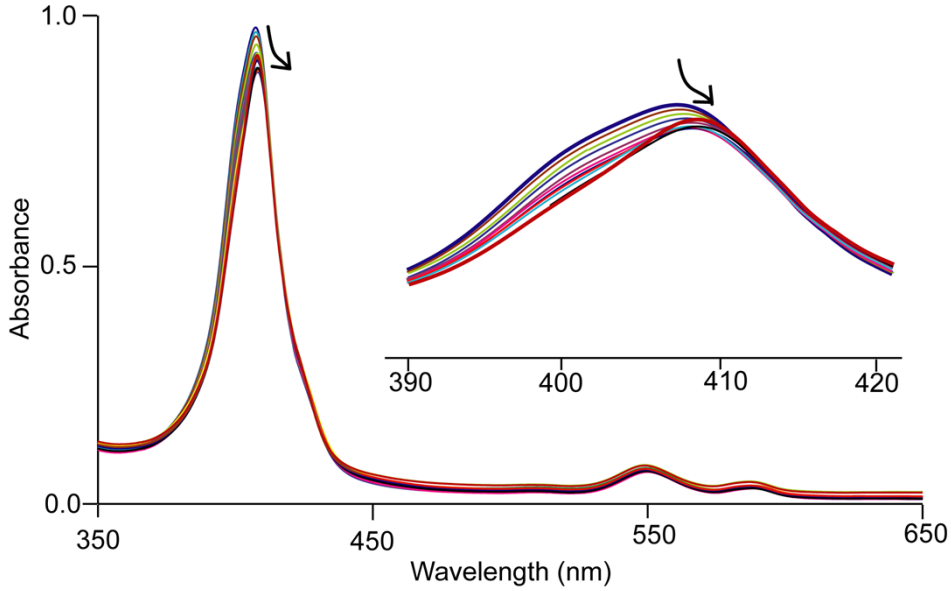

Figure S3. UV–visible spectral changes of **1** (5×10^{-6} M) in dichloromethane upon addition of DXN as the host: guest molar ratio changes from 1:0.1 to 1:72 at 295 K.

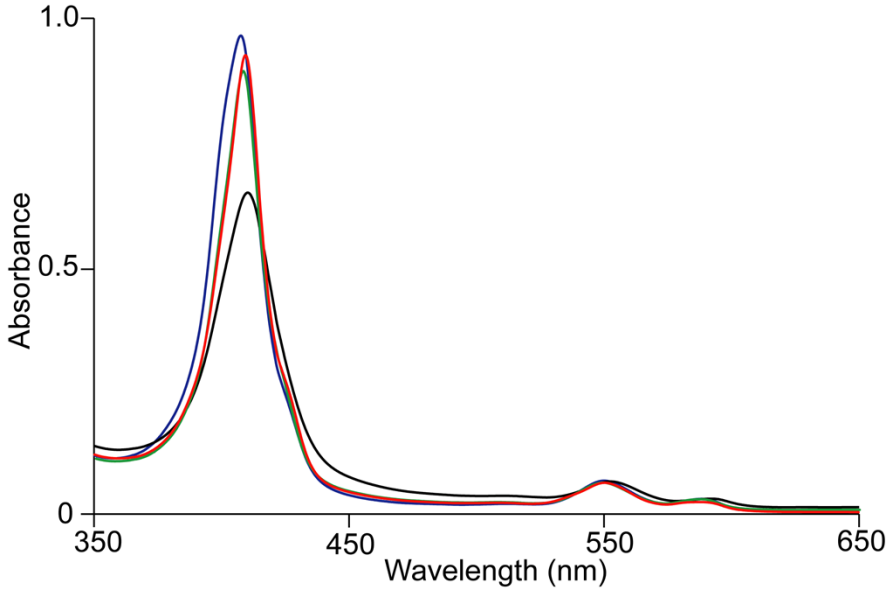

Figure S4. UV-visible spectra in dichloromethane for **1** (blue), **1**•PYMD (red), **1**•$(PYR)_2$ (black) and **1**•$(DXN)_2$ (green) at 295 K.

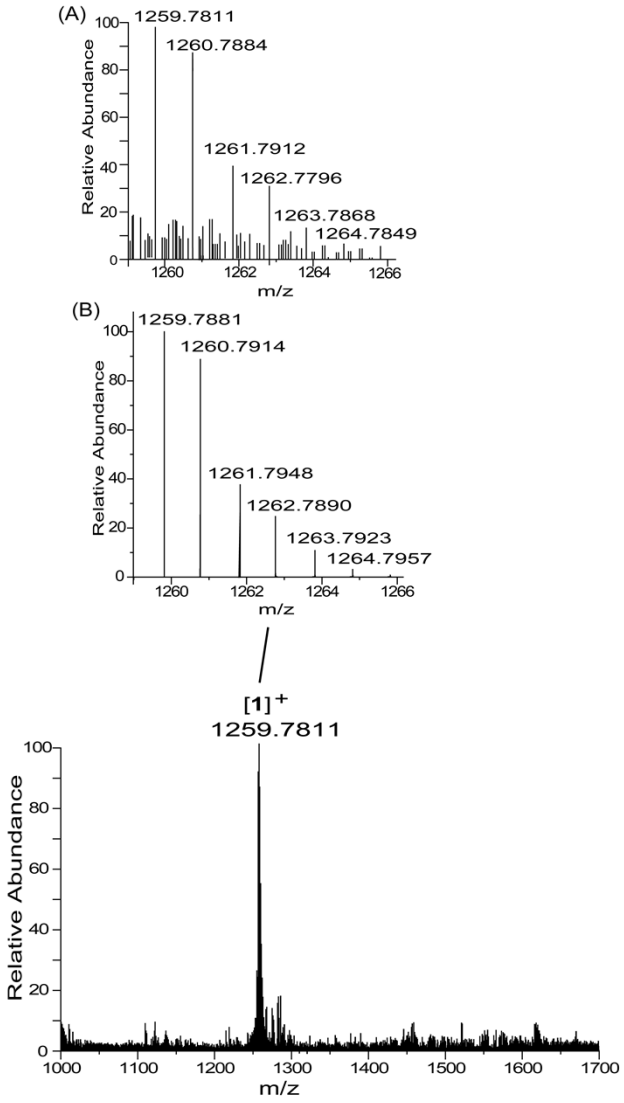

Figure S5. ESI-MS of **1**. Insets show isotopic distribution patterns, (A) experimental and (B) theoretical, for $[\mathbf{1}]^{+}$.

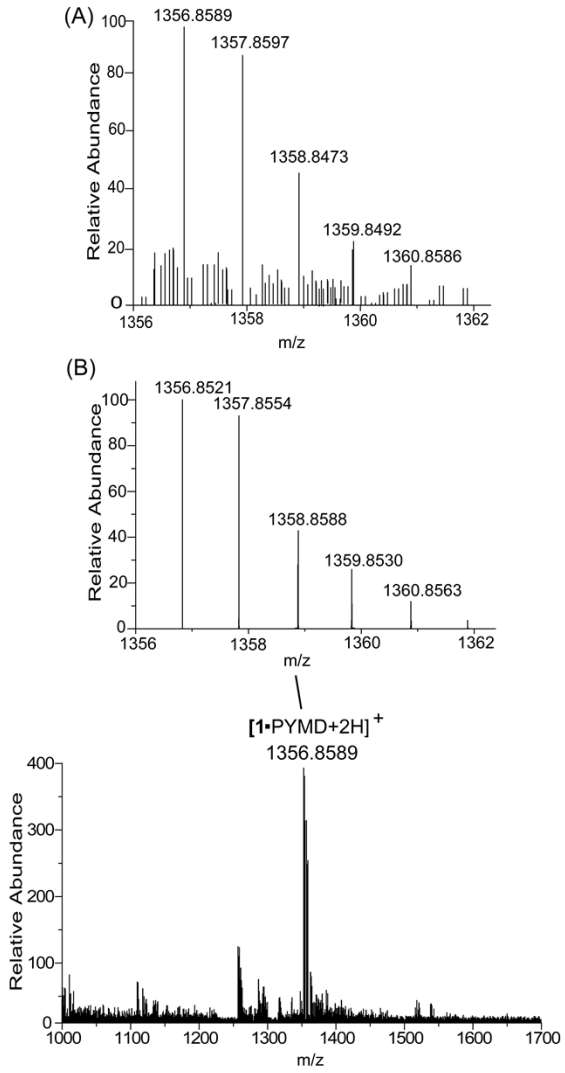

Figure S6. ESI-MS of **1**•PYMD. Insets show isotopic distribution patterns, (A) experimental and (B) theoretical, for [**1**•PYMD+2H]$^{+}$.

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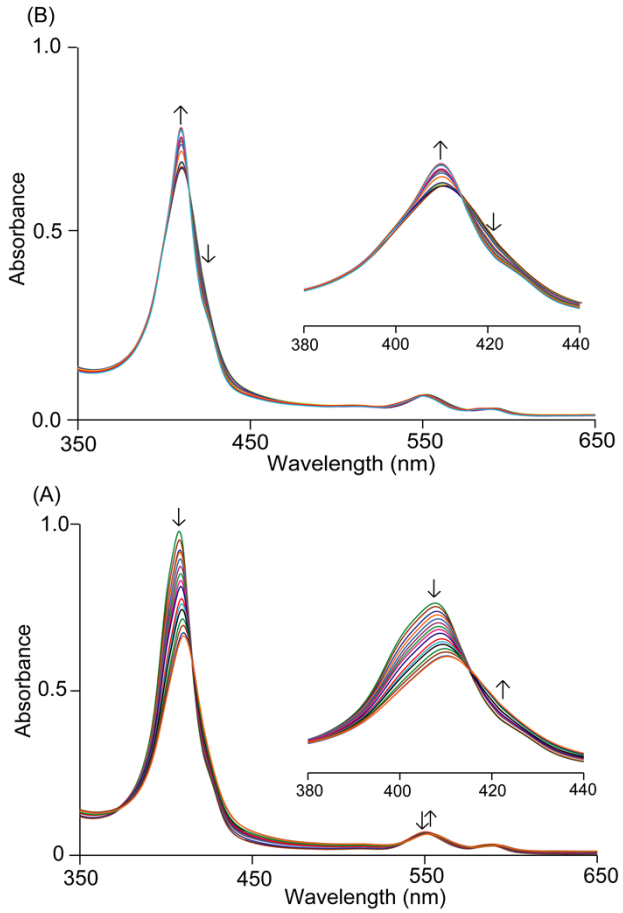

Figure S7. UV–visible spectral changes at 295K of (A) **1** (5×10^{-6} M) in dichloromethane upon addition of PYR as the host: guest molar ratio changes from 1:0.1 to 1:944 and (B) upon subsequent addition of PYMD on **1**•$(PYR)_2$ as the host: guest molar ratio changes from 1:0.1 to 1:15.

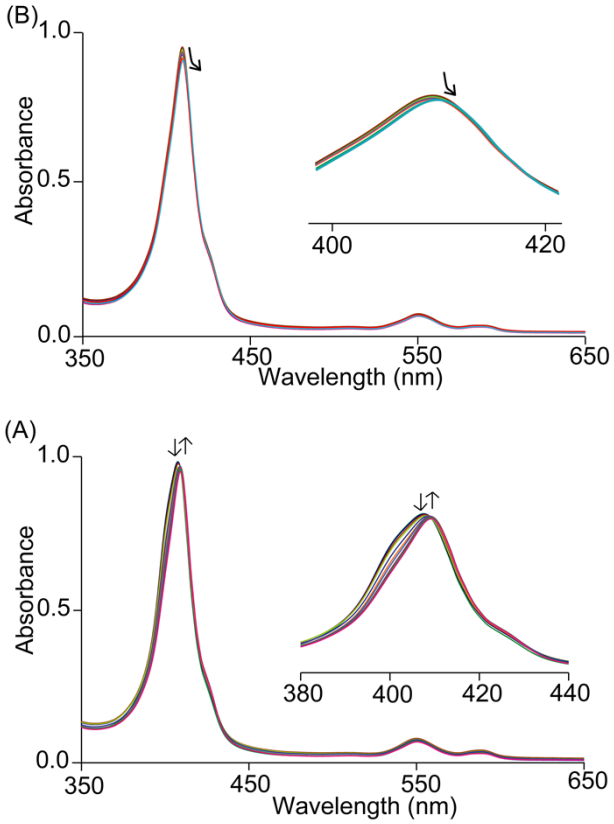

Figure S8. UV–visible spectral changes at 295K of (A) **1** (5×10^{-6} M) in dichloromethane upon addition of PYMD as the host: guest molar ratio changes from 1:0.1 to 1:5 and (B) upon subsequent addition of DXN on **1**•PYMD as the host: guest molar ratio changes from 1:0.1 to 1:380.

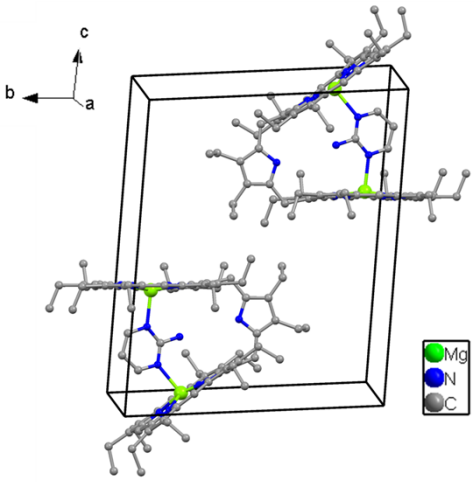

Figure S9. Diagram illustrating the packing of **1**•PYMD in the unit cell at 100 K (H-atoms, solvents chloroform and acetonitrile present in the crystal lattice have been omitted for clarity).

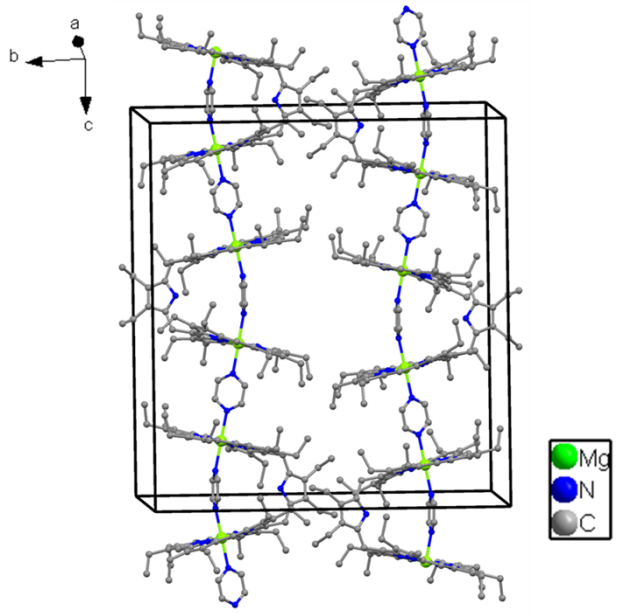

Figure S10. Diagram illustrating the 1-dimensional polymeric chain of **1**•$(PYR)_2$ in the unit cell at 100 K (H-atoms present in the crystal lattice have been omitted for clarity).

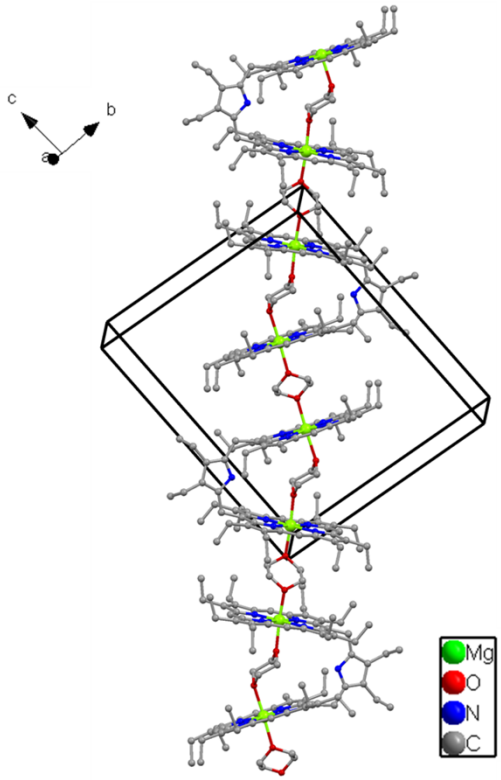

Figure S11. Diagram illustrating the 1-dimensional polymeric chain of **1**•$(DXN)_2$ in the unit cell at 100 K (H-atoms present in the crystal lattice have been omitted for clarity).

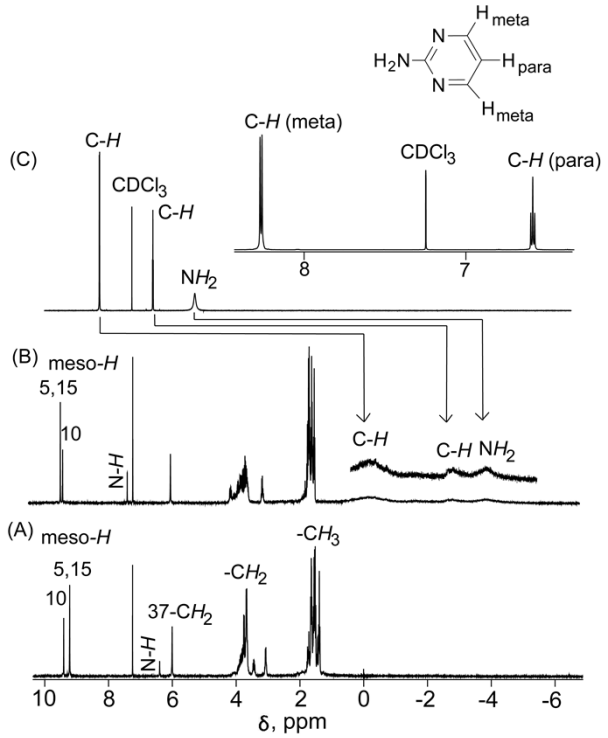

Figure S12. ^{1}H NMR spectra (in $CDCl_3$ at 295 K) of (a) **1**, (b) polycrystalline sample of **1**•PYMD and (c) PYMD. Inset shows the ligand protons.

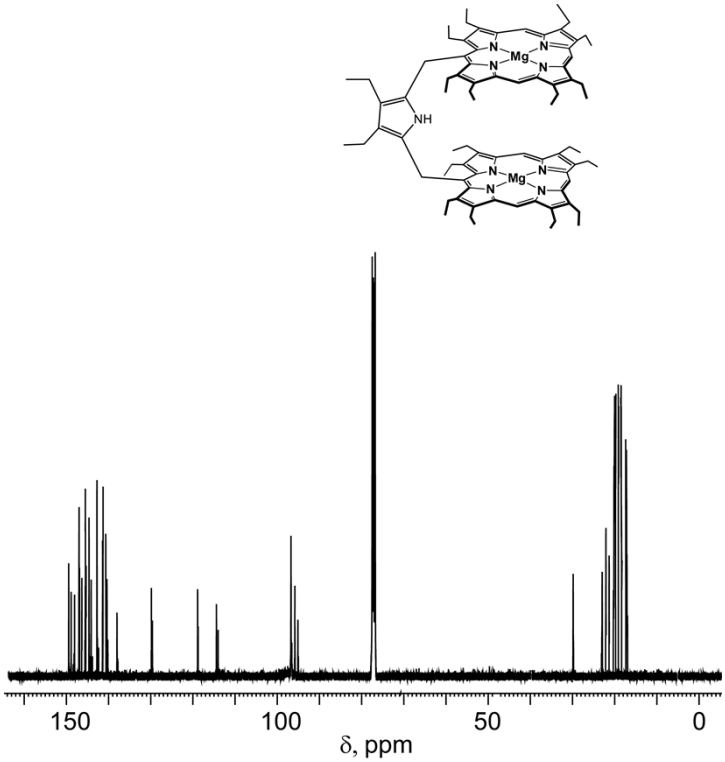

Figure S13. ^{13}C NMR spectrum of **1** (in $CDCl_3$, 295 K).

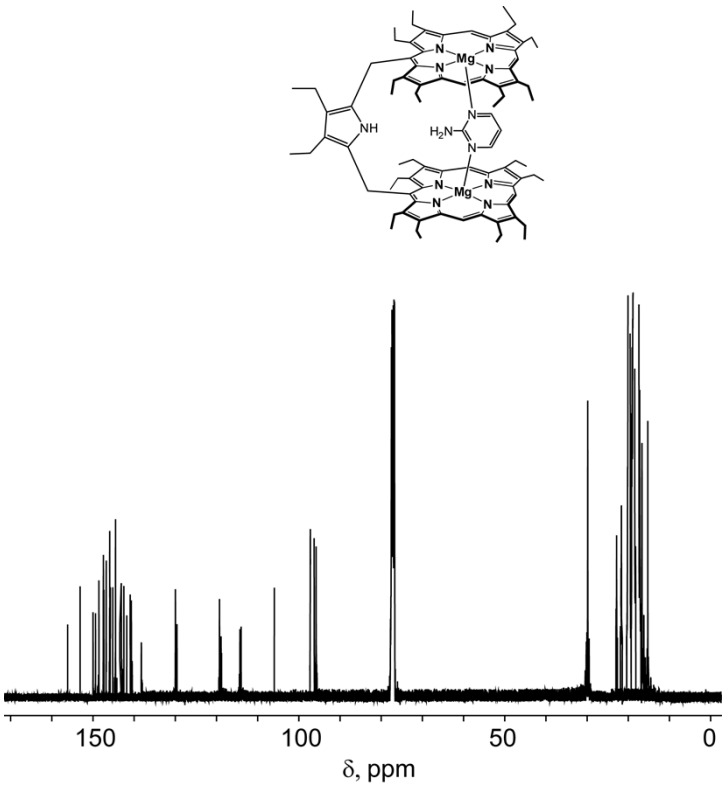

Figure S14. ^{13}C NMR spectrum of **1**•PYMD (in $CDCl_3$, 295 K).

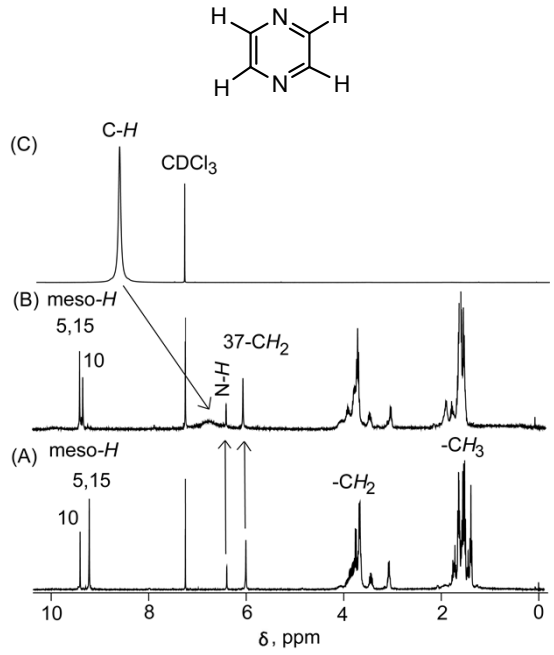

Figure S15. ^{1}H NMR spectra (in $CDCl_3$ at 295 K) of (a) **1**, (b) polycrystalline sample of **1**•$(PYR)_2$ and (c) PYR. Inset shows the ligand protons.

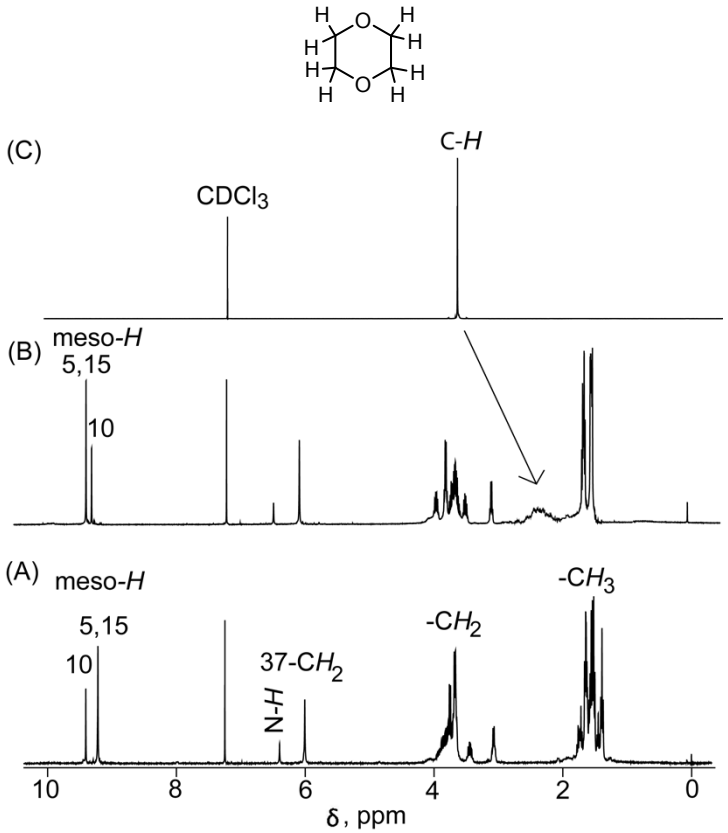

Figure S16. ^{1}H NMR spectra (in $CDCl_3$ at 295 K) of (a) **1**, (b) polycrystalline sample of **1**•$(DXN)_2$ and (c) DXN. Inset shows the ligand protons.

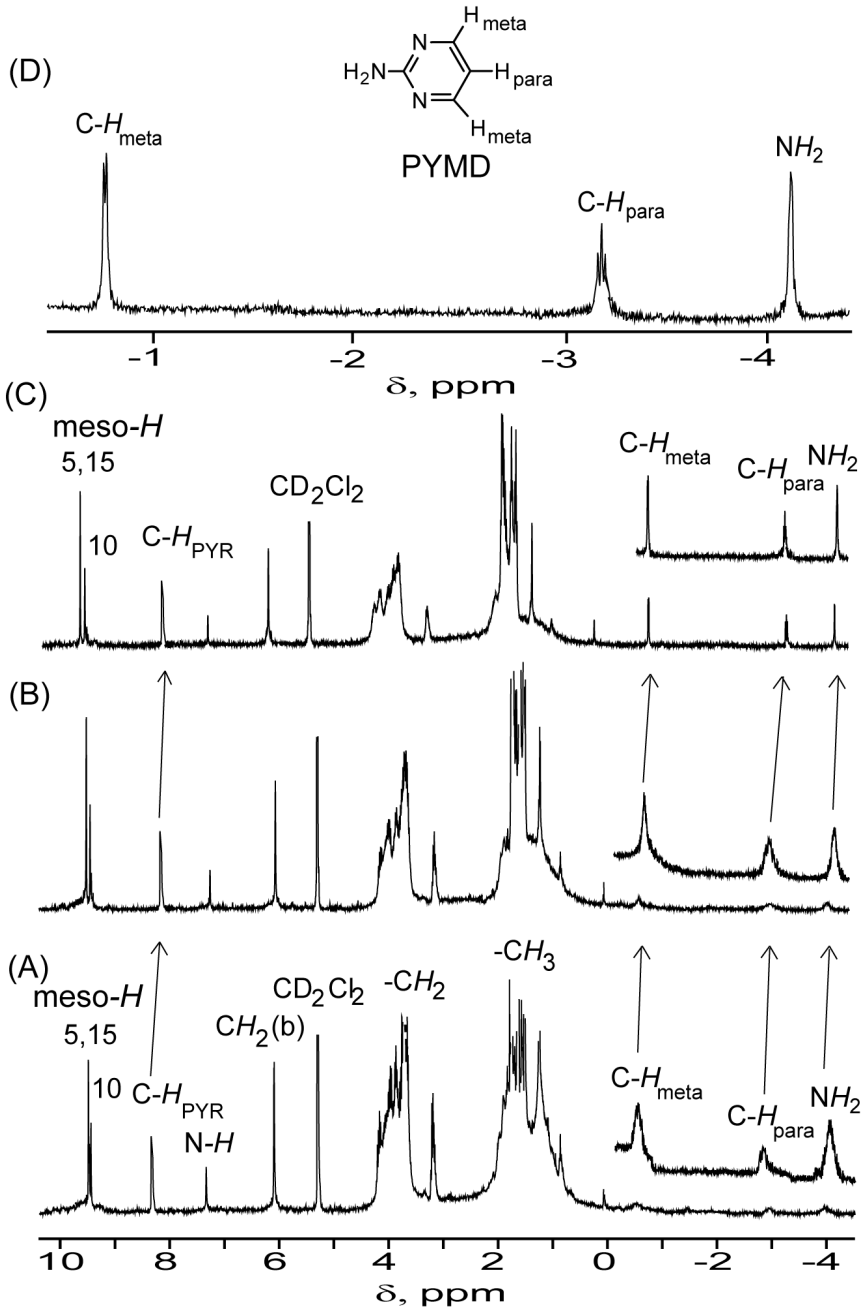

Figure S17. VT-^{1}H NMR spectra (in CD_2Cl_2) of **1**•PYMD•PYR at (A) 295 K, (B) 253 K, (C) 210 K and (D) Expanded ^{1}H NMR spectra at 210 K. Inset shows the ligand protons.

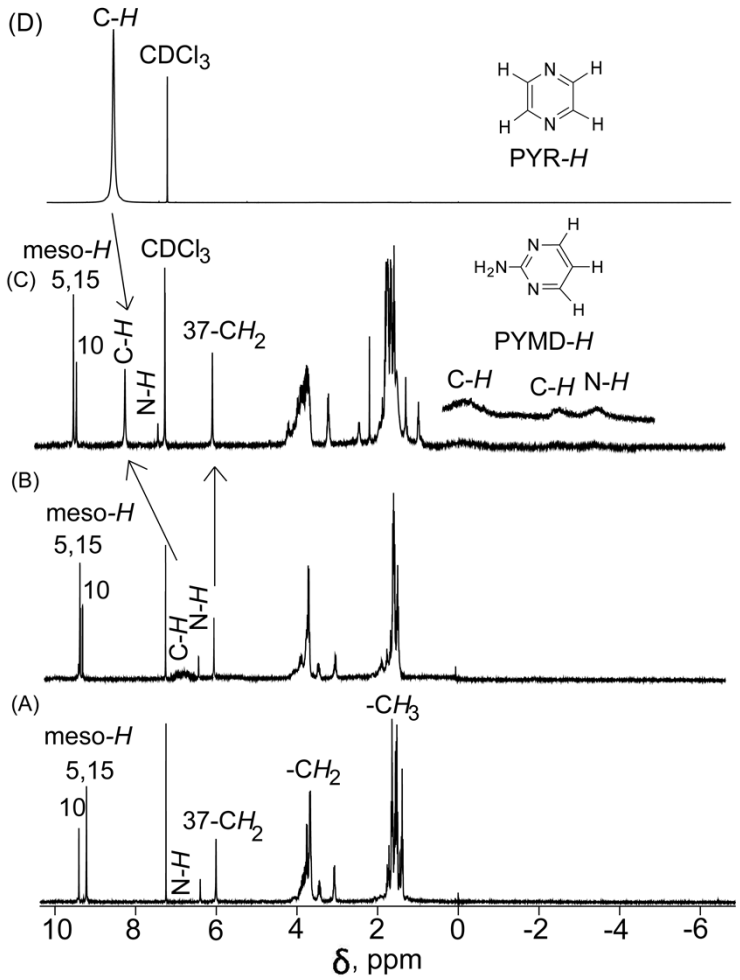

Figure S18. ^{1}H NMR spectra (in $CDCl_3$ at 295 K) of mixtures of **1**, PYR and PYMD at molar ratios of (A) 1:0:0, (B) 1:2:0, (C) 1:2:1 and (D) 0:0:1.

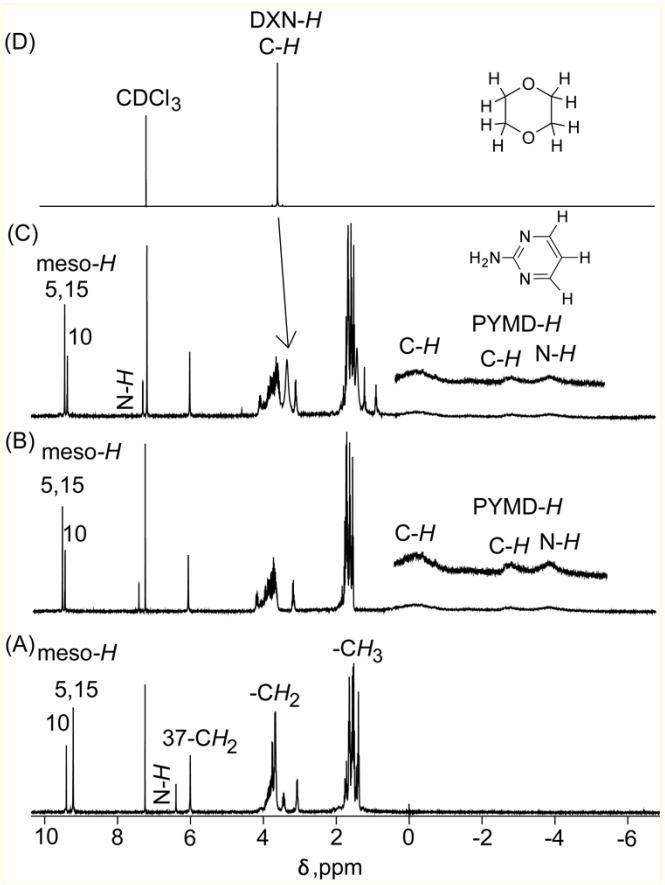

Figure S19. ^{1}H NMR spectra (in $CDCl_3$ at 295 K) of mixtures of **1**, PYMD and DXN at molar ratios of (A) 1:0:0, (B) 1:1:0, (C) 1:1:1 and (D) 0:0:1. Inset shows the ligand protons.

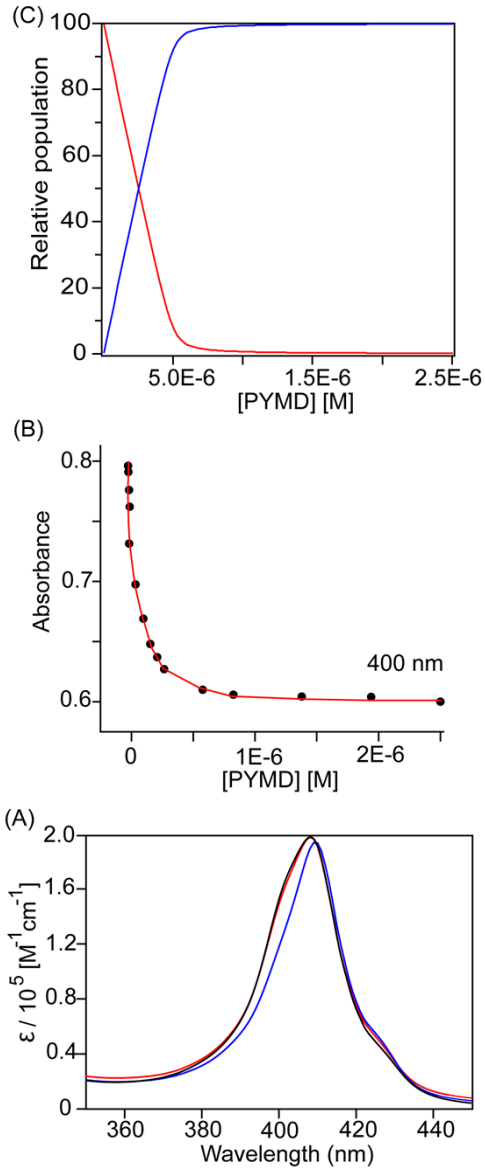

Figure S20. (A) Calculated UV-vis spectra of **1** (red), **1**•PYMD (blue). Black line represents the observed UV-visible spectra of **1**. (B) Fits of the absorbance data at selected wavelength of 400 nm. (C) Species distribution plots of **1**(red) and **1**•PYMD (blue).

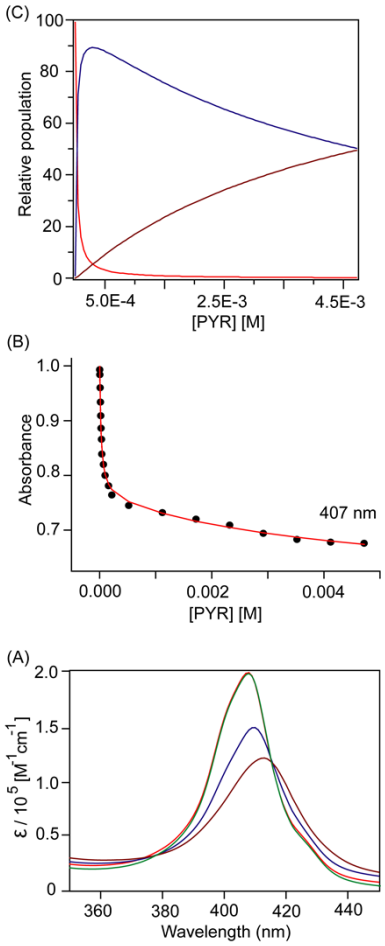

Figure S21. (A) Calculated UV-vis spectra of **1** (red), **1**•PYR (blue), and **1**•$(PYR)_2$ (brown). Green line represents the observed UV-visible spectra of **1**. (B) Fits of the absorbance data at selected wavelength of 407 nm. (C) Species distribution plots of **1** (red), **1**•PYR (blue) and **1**•$(PYR)_2$ (brown).

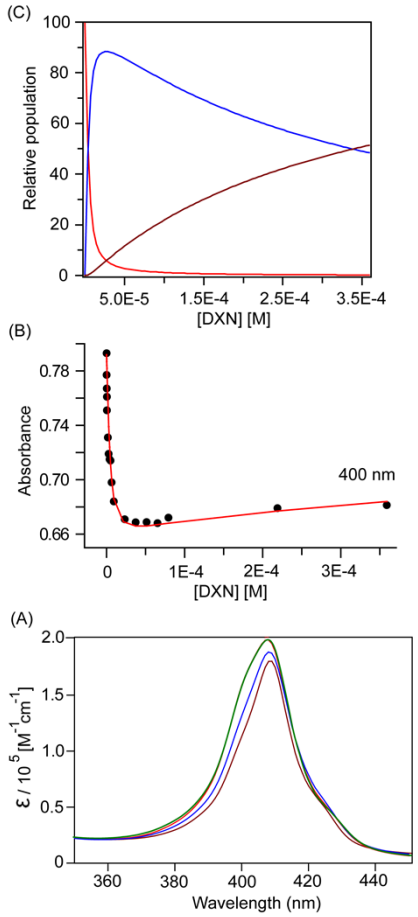

Figure S22. (A) Calculated UV-vis spectra of **1** (red), **1**•DXN (blue), and **1**•$(DXN)_2$ (brown). Green line represents the observed UV-visible spectra of **1**. (B) Fits of the absorbance data at selected wavelength of 400 nm. (C) Species distribution plots of **1** (red), **1**•DXN (blue) and **1**•$(DXN)_2$ (brown).

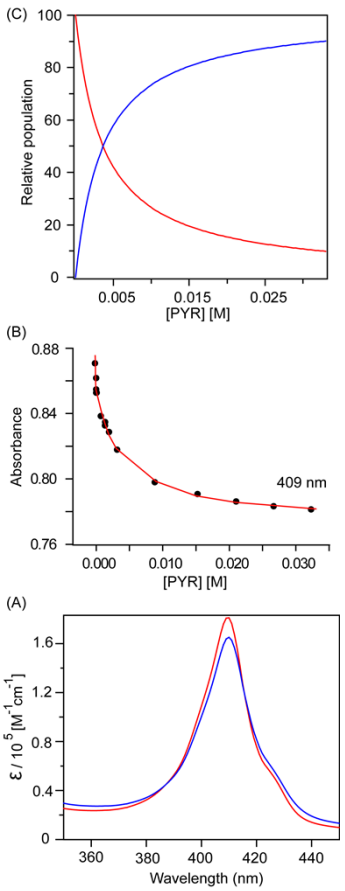

Figure S23. (A) Calculated UV-vis spectra of **1**•PYMD (red) and **1**•PYMD•PYR (blue). (B) Fits of the absorbance data at selected wavelength of 409 nm. (C) Species distribution plots of **1**•PYMD (red) and **1**•PYMD•PYR (blue).

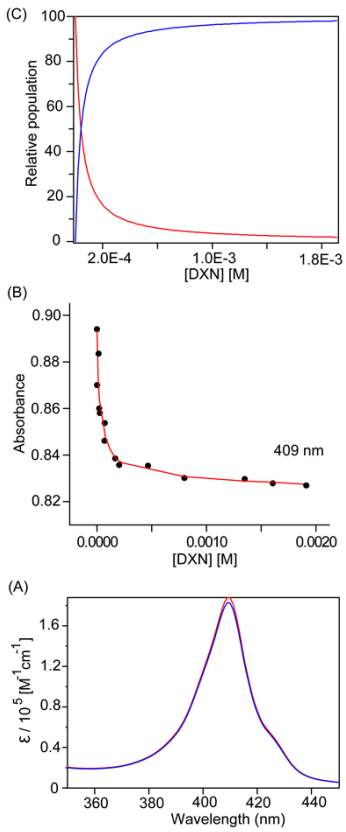

Figure S24. (A) Calculated UV-vis spectra of **1**•PYMD (red) and **1**•PYMD•DXN (blue). (B) Fits of the absorbance data at selected wavelength of 409 nm. (C) Species distribution plots of **1**•PYMD (red) and **1**•PYMD•DXN (blue).

Table S1. Selected bond lengths (Å) and bond angles (°) for the complexes.

Bond distance (Å)	**1**•PYMD	**1**•$(PYR)_2$	**1**•$(DXN)_2$	**1**•PYMD•DXN
Core-I				
Mg(1)-N(1)	2.073(3)	2.079(4)	2.073(3)	2.070(3)
Mg(1)-N(2)	2.093(4)	2.070(4)	2.080(3)	2.080(3)
Mg(1)-N(3)	2.090(4)	2.067(4)	2.079(3)	2.081(3)
Mg(1)-N(4)	2.070(4)	2.053(4)	2.080(3)	2.077(3)
Mg(1)-O(1)			2.163(3)	2.272(3)
Mg(1)-N(10)	2.233(4)	2.259(4)		2.447(3)
Core-II				
Mg(2)-N(5)	2.097(4)	2.068(4)	2.069(3)	2.066(3)
Mg(2)-N(6)	2.093(5)	2.069(4)	2.070(3)	2.078(3)
Mg(2)-N(7)	2.066(4)	2.052(4)	2.070(3)	2.074(3)
Mg(2)-N(8)	2.060(5)	2.062(4)	2.065(3)	2.078(3)
Mg(2)-O(2)			2.272(3)	2.229(3)
Mg(2)-N(11)	2.212(4)	2.244(4)		2.501(3)
Bond angle (º)				
Core-I				
N(1)–Mg1–N(2)	91.94(15)	91.71(15)	92.30(12)	92.71(12)
N(1)–Mg1–N(3)	163.72(16)	178.16(17)	179.65(13)	178.65(12)
N(1)–Mg1–N(4)	86.26(14)	87.89(15)	88.52(11)	87.43(11)
N(2)–Mg1–N(3)	85.33(14)	88.64(15)	87.84(12)	87.08(12)
N(2)–Mg1–N(4)	164.58(15)	177.62(17)	178.86(13)	176.70(12)
N(3)–Mg1–N(4)	92.11(15)	91.70(16)	91.33(12)	92.70(12)
Core-II				
N(5)–Mg2–N(6)	90.55(17)	91.59(15)	92.09(12)	92.14(12)
N(5)–Mg2–N(7)	163.88(18)	178.26(16)	179.20(14)	179.67(13)
N(5)–Mg2–N(8)	85.90(17)	88.10(14)	87.34(12)	87.87(11)
N(6)–Mg2–N(7)	86.03(18)	88.53(14)	88.34(12)	87.96(12)
N(6)–Mg2–N(8)	161.13(18)	179.49(17)	179.01(13)	177.22(12)
N(7)–Mg2–N(8)	92.27(18)	91.77(15)	92.24(12)	92.02(12)