Supporting Information

Solvent-Regulated Biomorphs from the Intense π,π-Mediated Assemblies of Tetracenequinone Fused Porphyrin

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1. Experimental Procedure

Genera

Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Thin-layer chromatography (TLC) was carried out on glass sheets coated with silica gel 60 F_{254} (Qingdao Haiyang Chemical Co., Ltd). ^{1}H NMR spectra were obtained using a Bruker AM 400 spectrometers, and the chemical shifts of ^{1}H were reported relative $CDCl_3$ (δ = 7.26), or D_8-toluene (δ = 2.08), while those of ^{13}C $CDCl_3$ (δ = 77.16), or D_8-toluene (δ = 20.43 for CD_3 of D_8-toluene). **Ni4TQ** and **Ni4AQ** both are highly symmetric, and the assignments are marked on a quarter of the molecules. UV-Vis absorption spectra were recorded on Shimadzu UV2600 spectrophotometer at room temperature. Mass data was obtained on the AB-4800plus MALDI-TOF mass spectrometer.

Crystallography

X-ray analyses were performed on a APEX-II equipped with a CCD detector (Bruker) using CuKa (graphite, monochromated, l = 1.54178 Å) radiation. The structures were solved by the direct method of SHELXS-2014 and refined using the SHELXL-2014 and Olex2 1.2 programs. The cif files of **Ni4AQ** (2082682), **Ni4TQ** (2082681) and another rough crystal structure of **Ni4TQ** grown from CS_2/*n*-hexane have been uploaded as SI of this manuscript.

Electrochemical Measurements

Cyclic voltametric (CV) and differential pulse voltametric (DPV) studies were carried out on a CorrTest Instrument Model CS350H with electrochemical system utilizing the three-electrode configuration consisting of a glassy carbon electrode (working electrode), platinum ring (counter electrode) and silver wire (reference electrode) in *o*-dichlorobenzene with *n*-tetrabutylammonium tetrafluoroborate ($TBABF_4$) as a supporting electrolyte. Potentials were calibrated with the ferrocene/ferrocenium couple as external standard.

Preparation of self-assembled microstructures

For the preparation of the samples, **Ni4TQ** was dissolved in a “good” solvent (THF or toluene) and subsequently a “bad” solvent (MeOH or isopropanol) was introduced. After 1 hour, the suspension solution was dropped on a mica slice and the remaining liquid was removed by filter paper stripes. For the case of assembly at 3:7 of THF:MeOH, **Ni4TQ** precipitated on the wall of the glass vail, thus the assemblies on the wall were pictured by SEM after 1 hour or 18 hours.

Scanning electron microscopy

For SEM observations the samples were covered with 10 nm Au sputtering and were observed directly. The SEM experiments were performed by using a S-3400N microscope operating at 15 kV.

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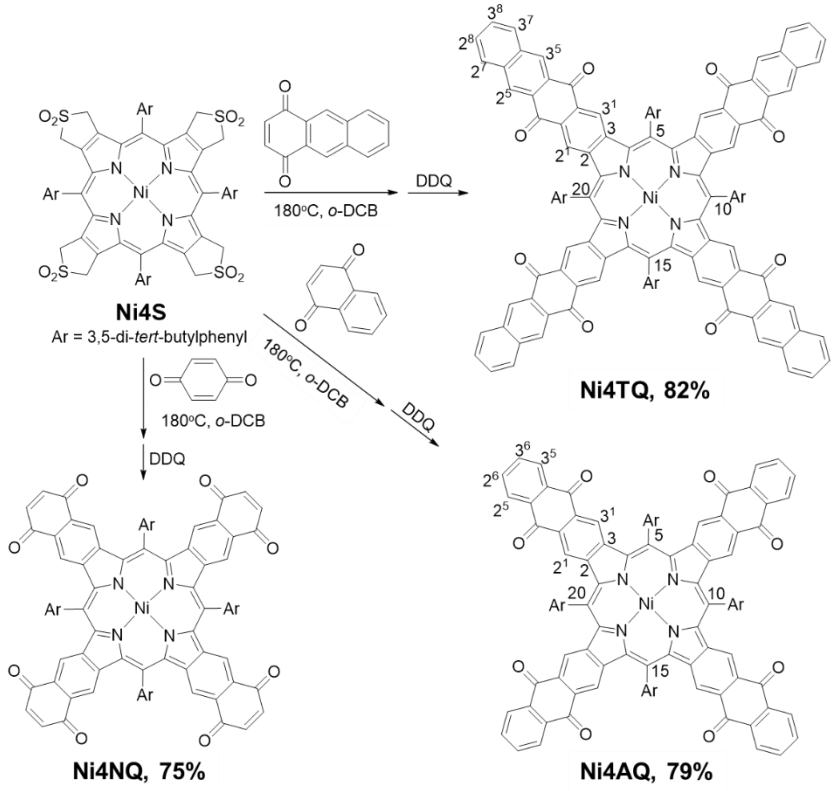
Synthesis



Synthesis of **Ni4TQ**

Ni4S[1] (30.0 mg, 20.26 μmol, 1 eq), AQ[2] (140 mg, 670.0 μmol, 33 eq), *o*-DCB (25 ml) were placed in a 50 ml round bottom flask and the air in the flask is replaced with argon. The reaction was heated to 180°C for 30 min and monitored by TLC until the reaction of raw material **Ni4S** is used up. DDQ (45 mg, 0.20 mmol, 10 eq) was added. After the reaction mixture was stirred at 110°C for 5 hours, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (3 × 30 ml). The combined organic layers were dried with Na_2SO_4, filtered, and evaporated under reduced pressure. The crude product dissolved in *o*-DCB was obtained, which was separated by chromatographic silica gel plate (CS_2/DCM = 2:1). Finally, **Ni4TQ** (34.0 mg, 82%) was obtained as a green powder after recrystallization from CS_2/hexane; M. p. > 300 °C; UV/Vis/NIR [toluene, λ_{max} (nm) ($\varepsilon \times 10^{-5}$/mol^{-1}dm^{3}cm^{-1})]: 704 (1.795), 513 (2.456); ^{1}H NMR (400 MHz, $CDCl_3/CS_2$): δ (ppm) = 8.86 (s, 8H), 8.35 (t, 4H, J = 1.7 Hz), 8.19 (s, 8H), 8.13 (dd, 8H, J = 2.9 Hz, J = 6.0 Hz), 7.90 (s, 8H, J = 1.7 Hz), 7.71 (dd, 8H, J = 2.9 Hz, J = 6.0 Hz), 1.55 (s, 72H, *t*-Bu-H); ^{1}H NMR (400 MHz, D^8-toluene): δ (ppm) = 8.75 (s, 8H), 8.71 (2, 4H), 8.57 (t, 4H, J = 1.6 Hz), 8.15 (d, 8H, J = 1.6 Hz), 7.44 (dd, 8H, J = 3.2 Hz, J = 2.8 Hz,), 7.10 (dd, 8H, *overlapped with toluene*), 1.65 (s, 72H, *t*-Bu-H); ^{13}C NMR (100 MHz, D^8-toluene, **Ni4TQ** is too insoluble to record a ^{13}C NMR spectrum, the ^{13}C data and partial assignments have been done on basis of the ^{1}H,^{13}C-HSQC and HMBC spectra): δ (ppm) = 182.1 (C2^3/C3^3), 142.8 (C2/C3), 135.2 (C2^6/C3^6), 131.1, 129.7 (C2^7/C3^7),

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129.4 (C2^5/C3^5), 128.7 (C2^8/C3^8), 127.4, 127.2 (*ortho*-Ar), 125.1 (C2^1/C3^1), 124.6 (*para*-Ar), 119.3, 35.7, 31.6; MS (MALDI-TOF) *m*/*z* : [M$^+$] Calculated for $C_{140}H_{116}N_4NiO_8$ 2038.8; found 2038.6.

Synthesis of **Ni4AQ**

Ni4S[1] (10.0 mg, 6.75 μmol, 1 eq), NQ (53.3 mg, 337.5 μmol, 50 eq), *o*-DCB (10 ml) were placed in a 25 ml round bottom flask and the air in the flask is replaced with argon. The reaction was heated to 180ºC for 30 min and monitored by TLC until the reaction of raw material **Ni4S** is used up. DDQ (15 mg, 66.0 μmol, 10 eq) was added. After the reaction mixture was stirred at 110ºC for 5 hours, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (3 × 30 ml). The combined organic layers were dried with Na_2SO_4, filtered, and evaporated under reduced pressure. The crude product dissolved in *o*-DCB was obtained, which was diluted with PE (10 ml) and separated by column chromatography. First, the *o*-DCB is washed down with PE, and the polarity is increased slowly to DCM:PE=2:1. **Ni4AQ** was obtained (9.8 mg, 79%, green solid) after recrystallization of DCM / hex; M.p. > 300 ºC; UV/Vis/NIR [toluene, λ_{max} (nm) ($\varepsilon \times 10^{-5}$/mol^{-1}dm^{3}cm^{-1})]: 705 (1.615), 516 (1.933); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.34 (dd, 8H, *J* = 3.3 Hz, *J* = 5.7 Hz), 8.23 (t, 4H, *J* = 1.4 Hz), 8.12 (s, 8H), 7.86 (d, 8H, *J* = 1.4 Hz), 7.78 (dd, 8H, *J* = 3.3 ppm, *J* = 5.7 Hz), 1.49 (s, 72H, *t*-Bu-H); ^{13}C NMR (100 MHz, $CDCl_3$, partial assignments have been done on basis of the ^{1}H,^{13}C-HSQC-spectrum): δ (ppm) = 182.7 (C2^3/C3^3), 152.7, 142.5, 138.2, 137.0, 134.5, 133.8 (C2^6/C3^6), 129.5, 127.3 (C2^5/C3^5), 127.1 (*ortho*-Ar), 124.7 (C2^1/C3^1), 124.3 (*para*-Ar), 119.0, 35.5, 31.7; MS (MALDI-TOF) *m*/*z* : [M$^+$] Calculated for $C_{124}H_{108}N_4NiO_8$ 1838.8; found 1838.6.

Synthesis of **Ni4NQ**

Ni4S[1] (10.0 mg, 6.75 μmol, 1 eq), BQ (25.5 mg, 235.9 μmol, 35 eq), *o*-DCB (10 ml) were placed in a 25 ml round bottom flask and the air in the flask is replaced with argon. The reaction was heated to 180ºC for 30 min and monitored by TLC until the reaction of raw material **Ni4S** is used up. DDQ (15.0 mg, 66.0 μmol, 10 eq) was added. After the reaction mixture was stirred at 110ºC for 5 hours, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (3 × 30 ml). The combined organic layers were dried with Na_2SO_4, filtered, and evaporated under reduced pressure. The crude product dissolved in *o*-DCB was obtained, which was diluted with PE (10 ml) and separated by column chromatography. First, the *o*-DCB is washed down with PE, and the polarity is increased slowly to DCM:PE=1:1. **Ni4NQ** was obtained (5.3 mg, 75%, green solid) after recrystallization of DCM / hex; M.p. > 300 ºC; UV/Vis/NIR [toluene, λ_{max} (nm) ($\varepsilon \times 10^{-5}$/mol^{-1}dm^{3}cm^{-1})]: 714 (1.252), 526 (1.135); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.15 (t, 4H, *J* = 1.6 Hz), 8.83 (s, 8H), 7.77 (d, 8H, *J* = 1.6 Hz), 6.94 (s, 8H), 1.44 (s, 72H, *t*-Bu-H). The data is consistence with the reported data.[3]

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2. NMR and Mass Spectra

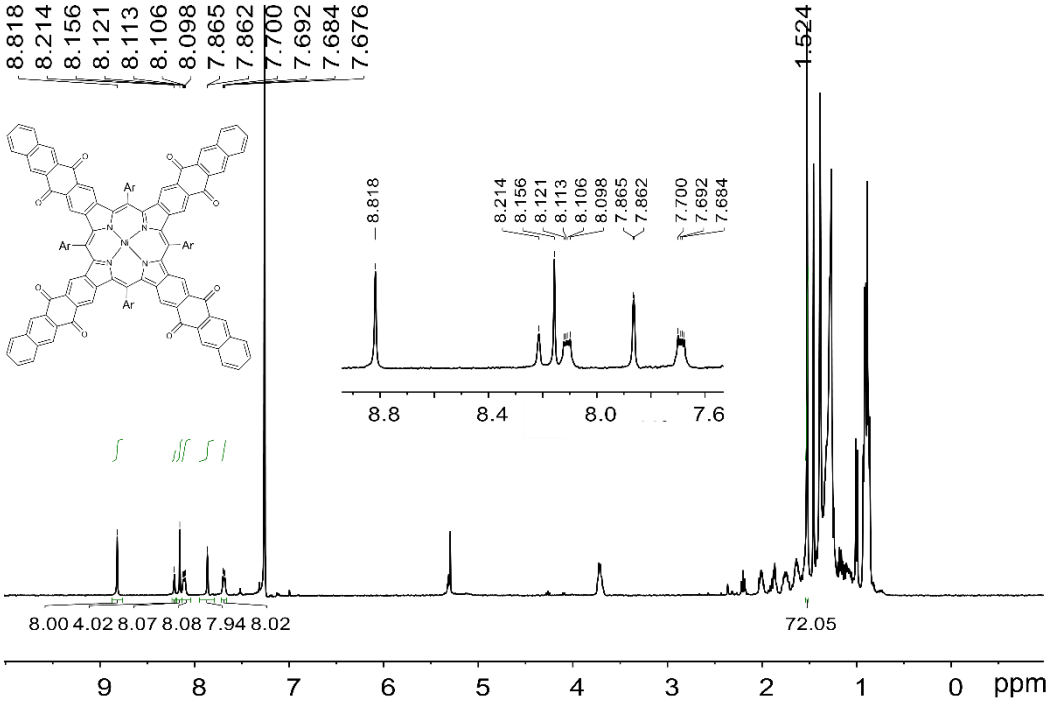

Figure S1. ^{1}H NMR spectrum of Ni4TQ in $CDCl_3/CS_2$ (298 K, 400MHz).

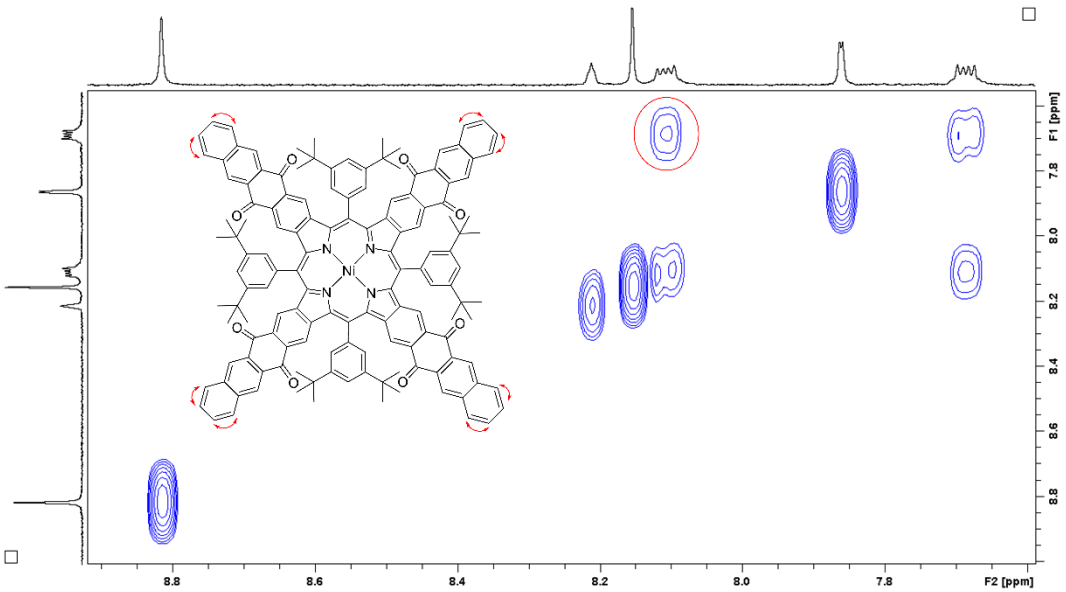

Figure S2. ^{1}H,^{1}H-COSY spectrum of Ni4TQ in $CDCl_3/CS_2$ (298 K, 400MHz).

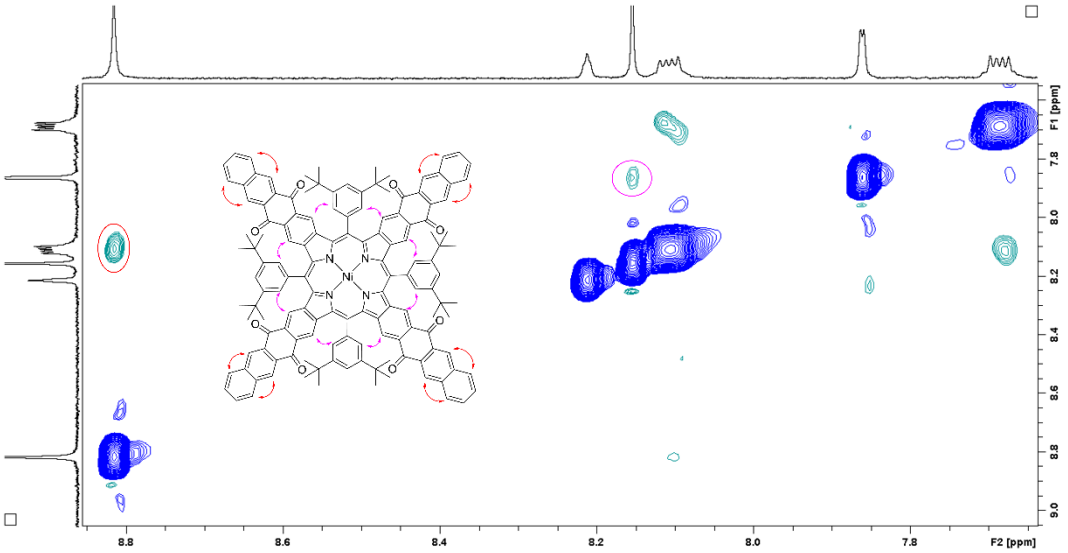

Figure S3. ^{1}H,^{1}H-ROESY spectrum of Ni4TQ in $CDCl_3/CS_2$ (298 K, 400MHz).

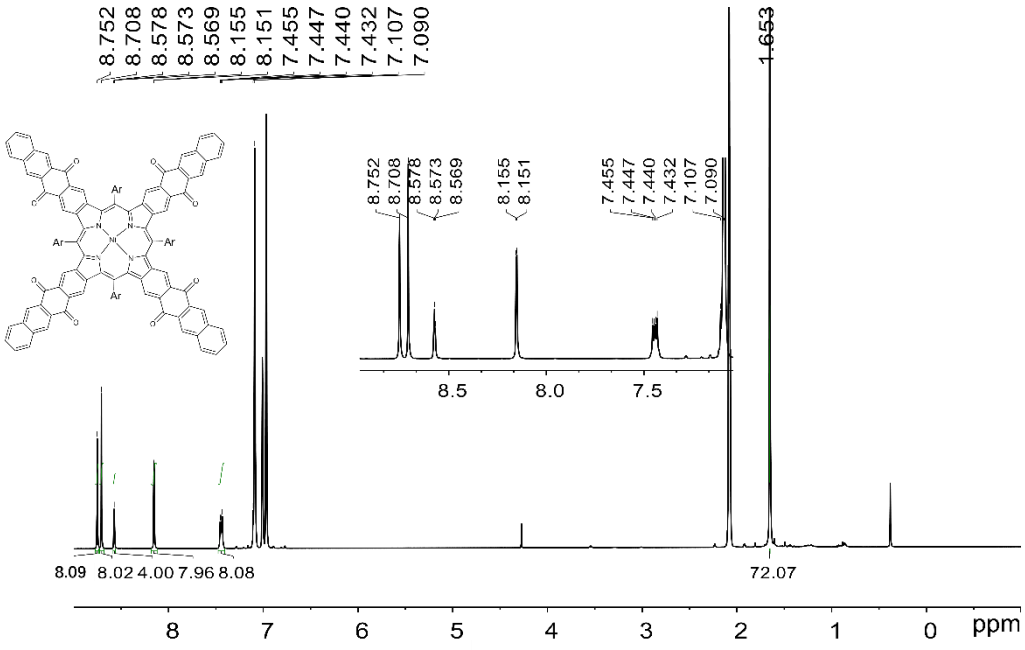

Figure S4. ^{1}H NMR spectrum of Ni4TQ in D^{8}-toluene (298 K, 400MHz).

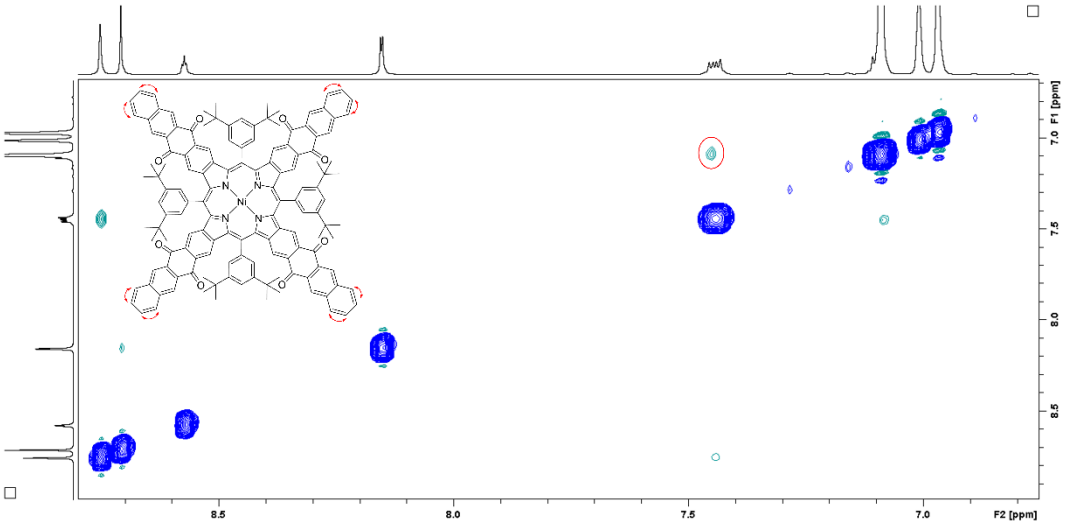

Figure S5. ^{1}H,^{1}H-ROESY spectrum of Ni4TQ in D^{8}-toluene (298 K, 400MHz).

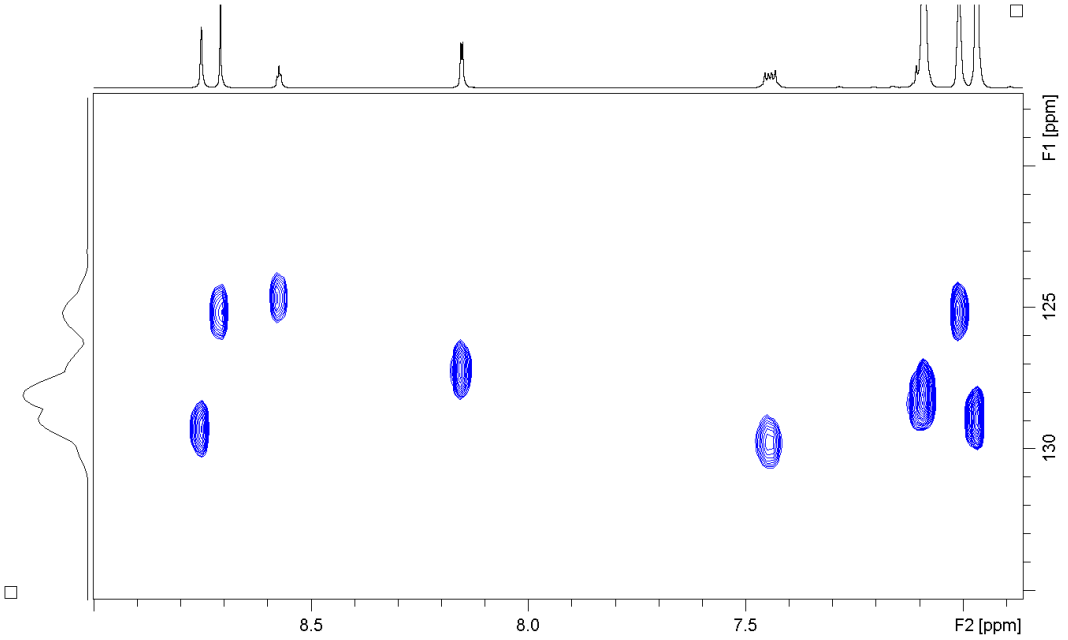

Figure S6. ^{1}H,^{13}C-HSQC spectrum of Ni4TQ in D^{8}-toluene (298 K, 400MHz).

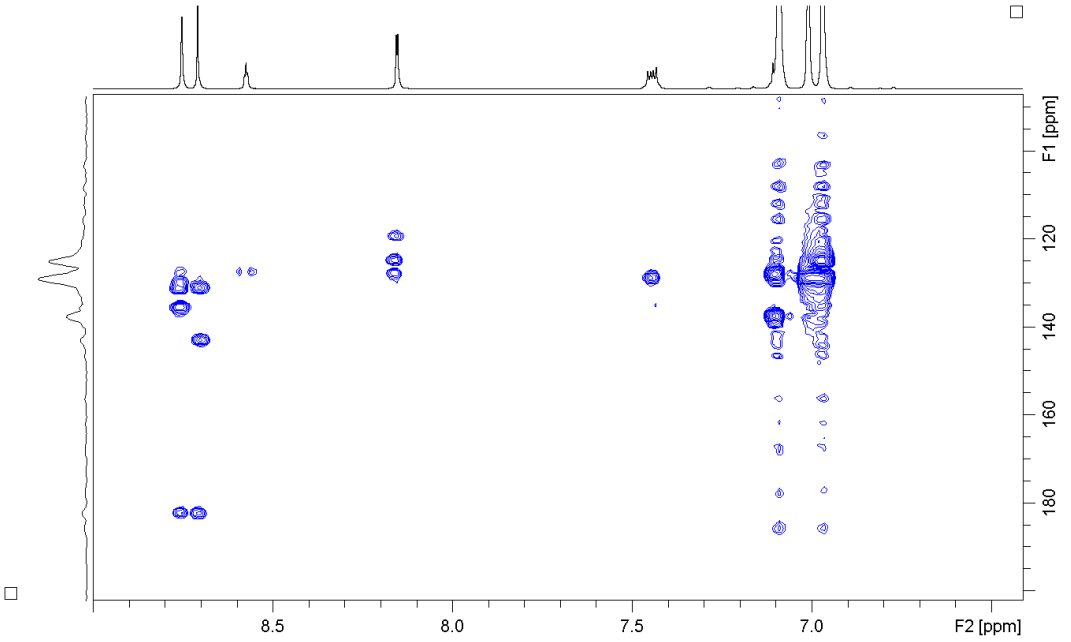

Figure S7. $^{1}H,^{13}C$-HMBC spectrum of Ni4TQ in D^{8}-toluene (298 K, 400MHz).

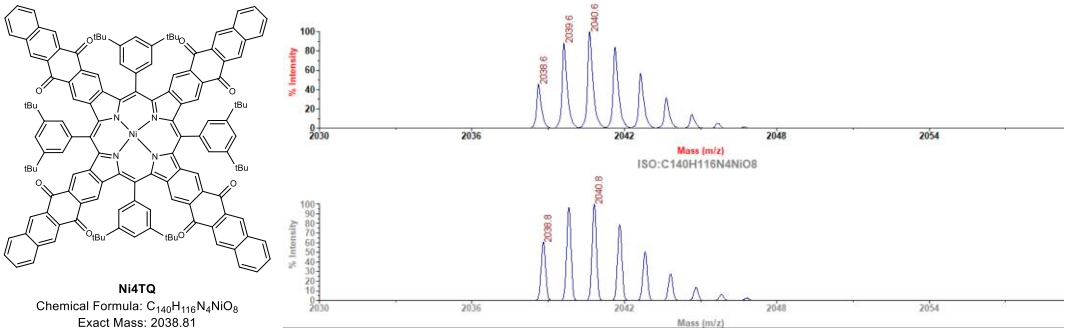

Figure S8. MS (MALDI-TOF) of Ni4TQ.

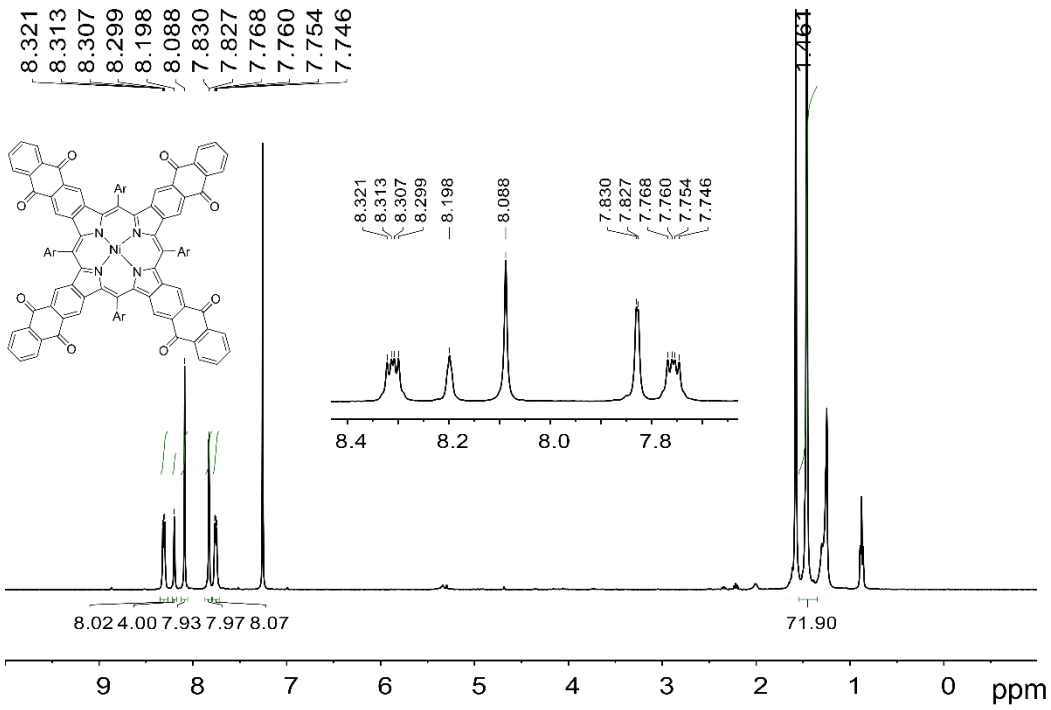

Figure S9. ^{1}H NMR spectrum of Ni4AQ in $CDCl_3$ (298 K, 400MHz).

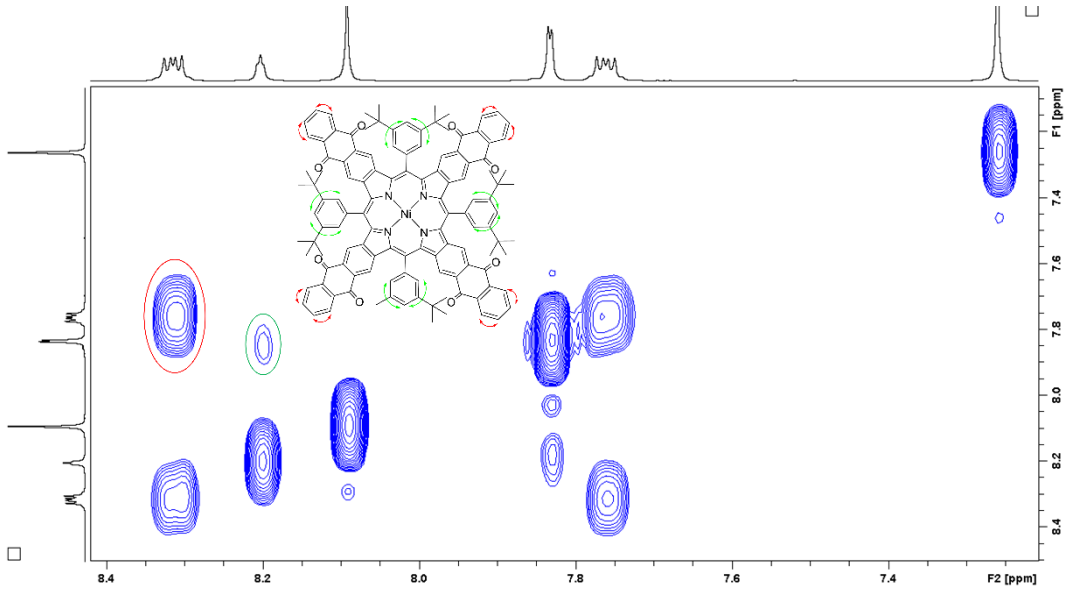

Figure S10. ^{1}H,^{1}H-COSY spectrum of Ni4AQ in $CDCl_3$ (298 K, 400MHz).

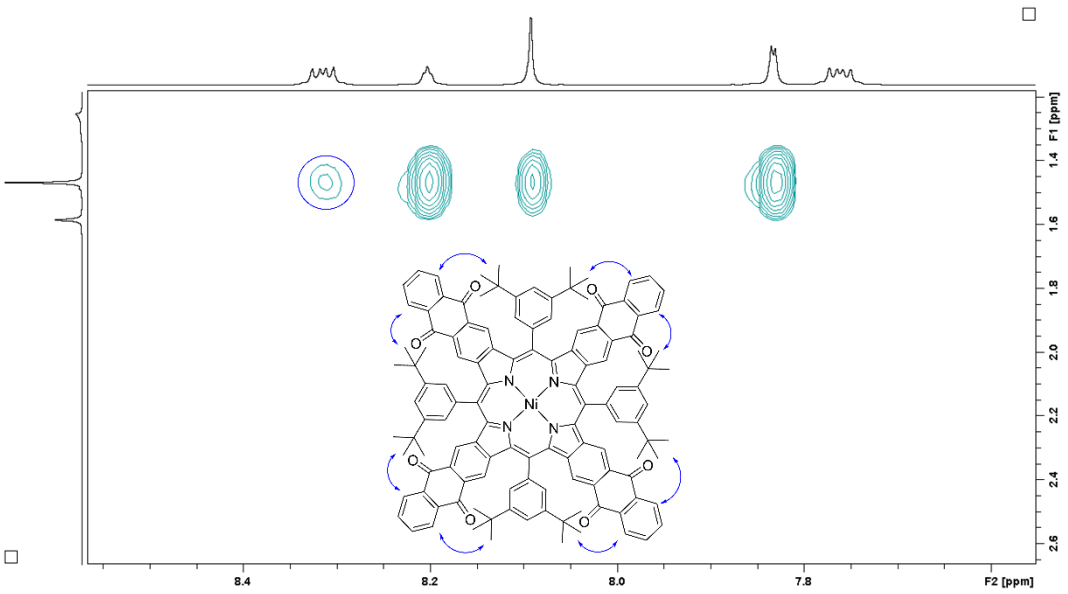

Figure S11. ^{1}H,^{1}H-ROESY spectrum of Ni4AQ in $CDCl_3$ (298 K, 400MHz).

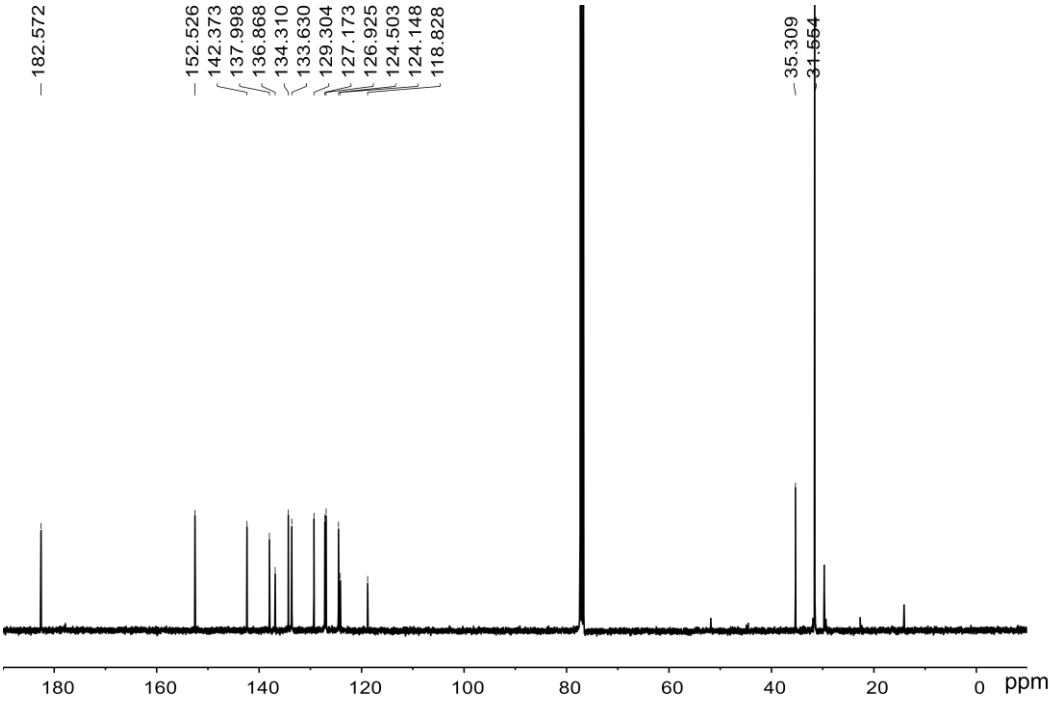

Figure S12. ^{13}C NMR spectrum of Ni4AQ in $CDCl_3$ (298 K, 100MHz).

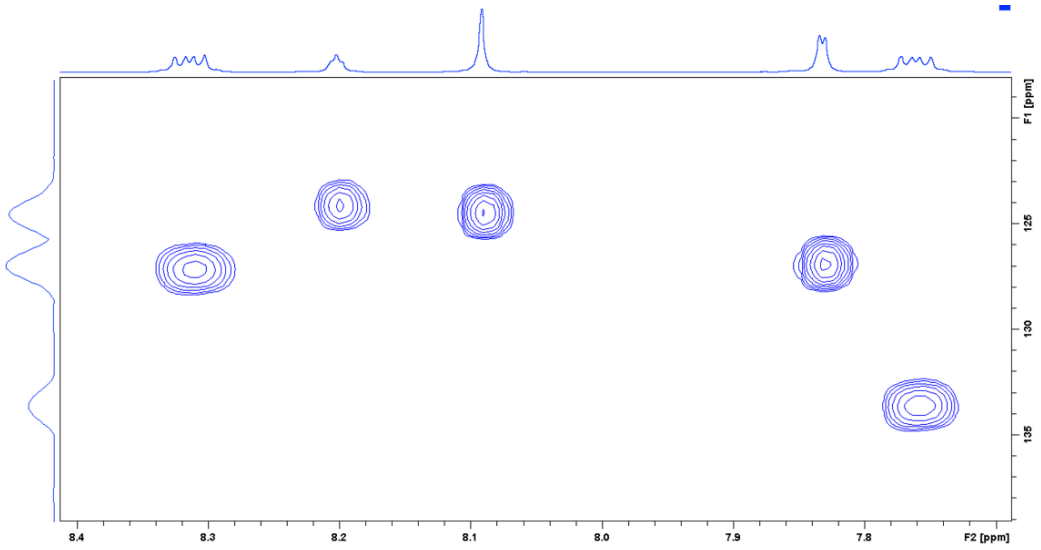

Figure S13. $^{1}H,^{13}C$-HSQC spectrum of Ni4AQ in $CDCl_3$ (298 K, 400MHz).

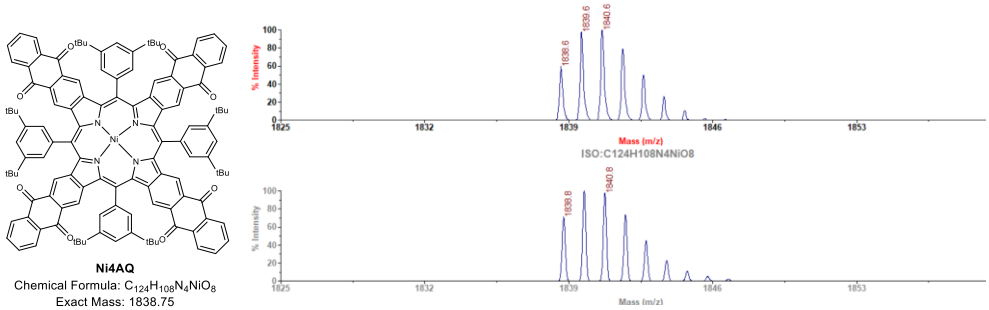

Figure S14. MS (MALDI-TOF) of Ni4AQ.

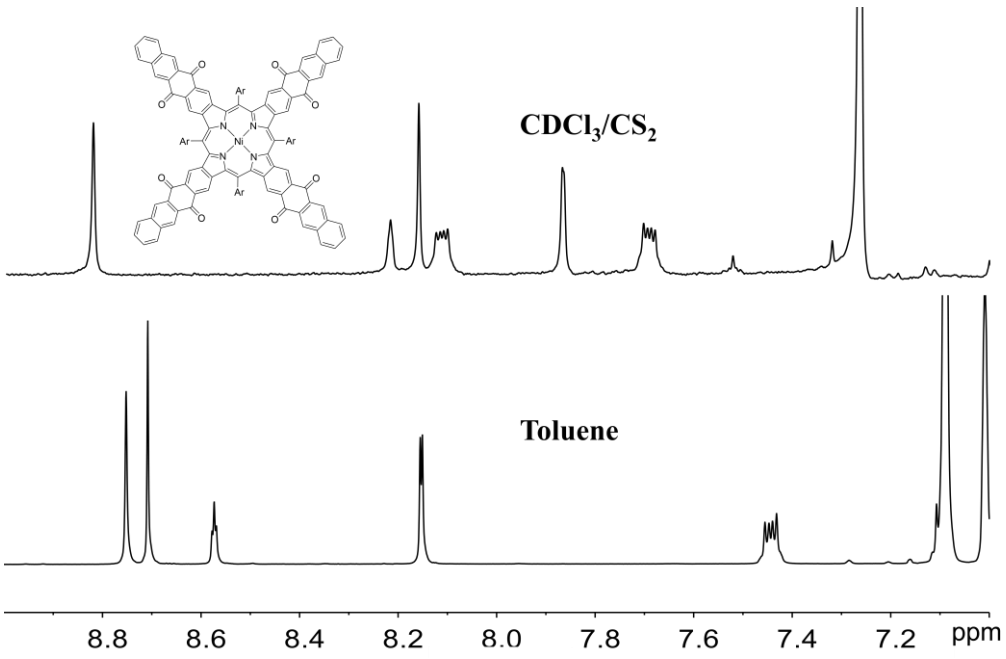

Figure S15. ^{1}H NMR spectra of Ni4TQ in $CDCl_3/CS_2$ and D^{8}-toluene (298 K, 400MHz).

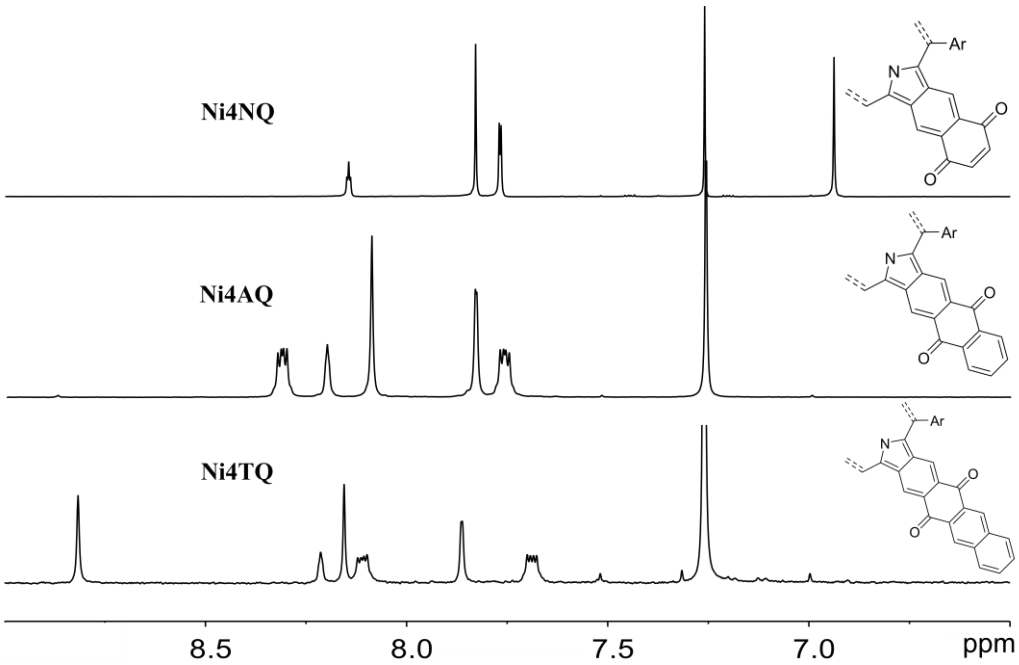

Figure S16. ^{1}H NMR spectra of Ni4TQ, Ni4AQ and Ni4NQ in $CDCl_3$ (298 K, 400MHz, partial structures are shown).

3. Absorption Spectra and Electrochemical Data

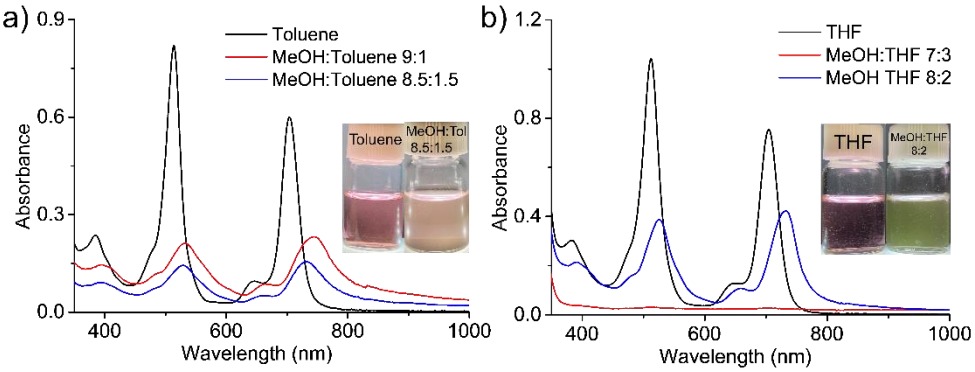

Figure S17. Absorption spectra of Ni4TQ in toluene and in the mixture of toluene/MeOH (a) and in THF and in the mixture of THF/MeOH (b) with pictures of solution color under white light. The green color for suspension solution seems to result from the scattering effect of the nano/microscale structures.

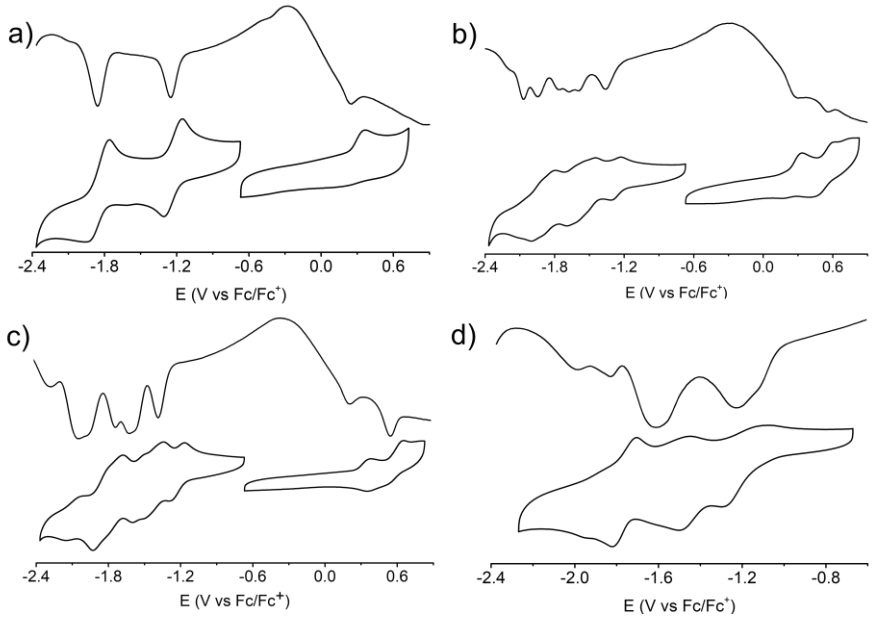

Figure S18. CV and DPV data of Ni4S (a), Ni4TQ (b), Ni4AQ (c) and Ni4NQ (d).

Table S1. DPV data of Ni4S, Ni4TQ, Ni4AQ and Ni4NQ in *o*-dichlorobenzene measured with ferrocene as external standard. HOMO-LUMO energy gap (ΔH-L) = e ($E_{ox}1$ - $E_{red}1$).

Compound	Reduction (V)							Oxidation (V)		ΔH-L (eV)
	$E_{red}7$	$E_{red}6$	$E_{red}5$	$E_{red}4$	$E_{red}3$	$E_{red}2$	$E_{red}1$	$E_{ox}1$	$E_{ox}2$	
Ni4S	—	—	—	—	—	-1.86	-1.25	0.25	—	1.50
Ni4TQ	-2.05	-1.92	-1.80	-1.63	-1.55	-1.47	-1.25	0.33	0.57	1.58
Ni4AQ	-2.07	-1.85	-1.79	-1.56	-1.45	-1.41	-1.23	0.27	0.59	1.50
Ni4NQ	—	—	-1.98	-1.82	-1.61	-1.22	-1.11	0.27	0.60	1.38

4. SEM images and Crystal structures

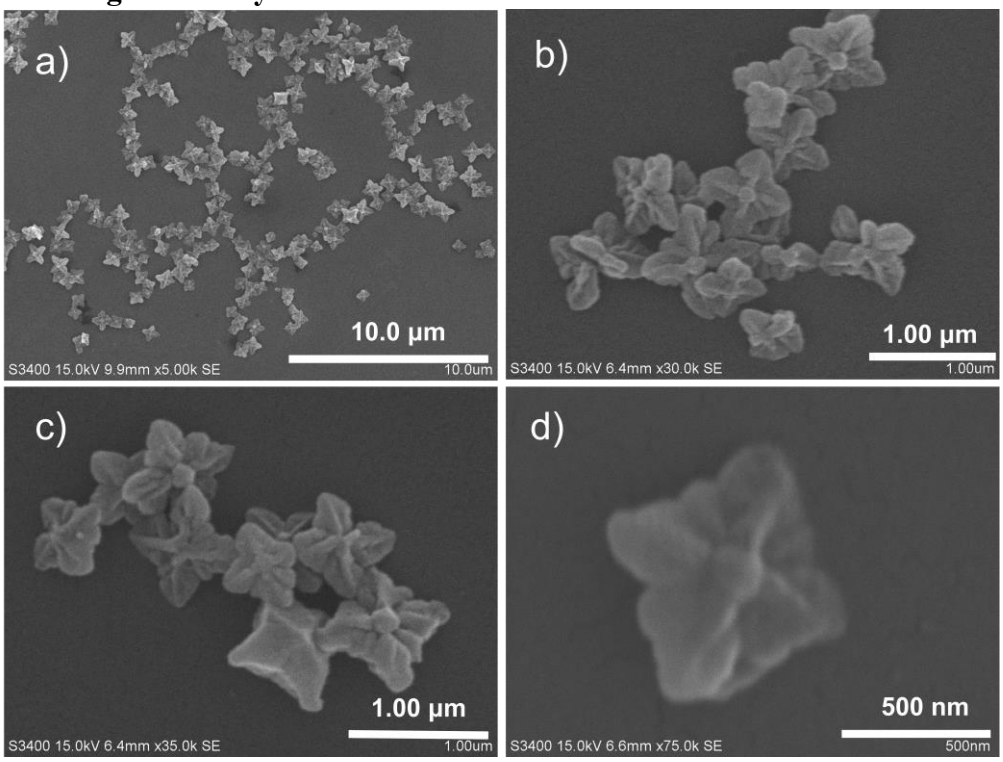

Figure S19. SEM of Ni4TQ assemblies obtained from MeOH:toluene = 9:1 with final concentration of ~5 µM.

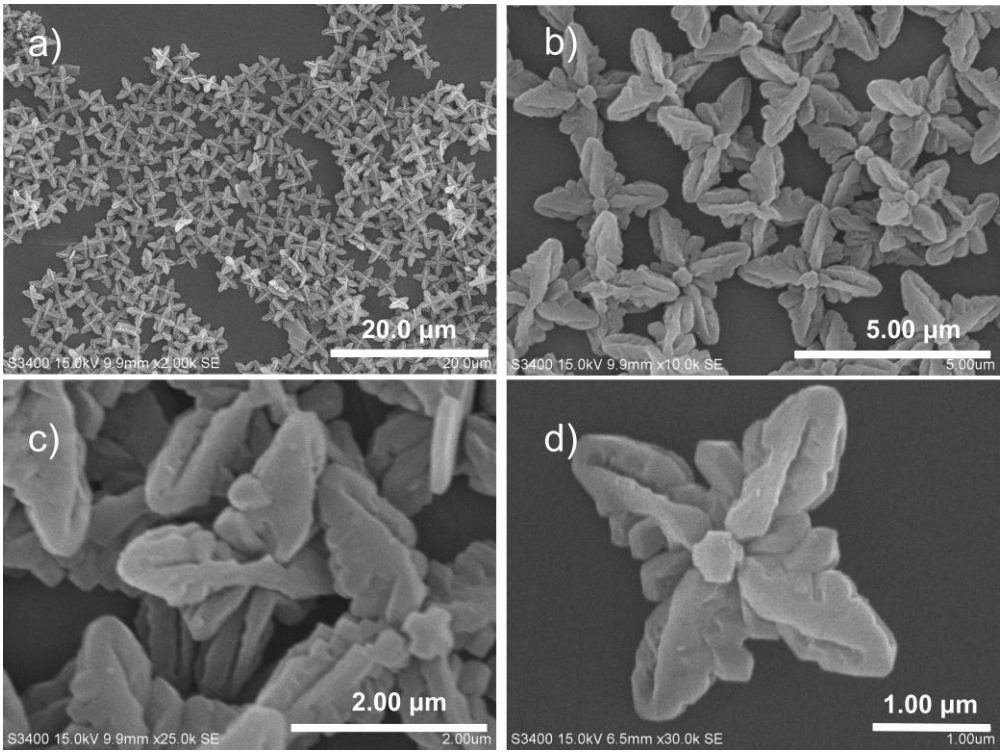

Figure S20. SEM of Ni4TQ assemblies obtained from MeOH:toluene = 8.5:1.5 with final concentration of ~5 µM.

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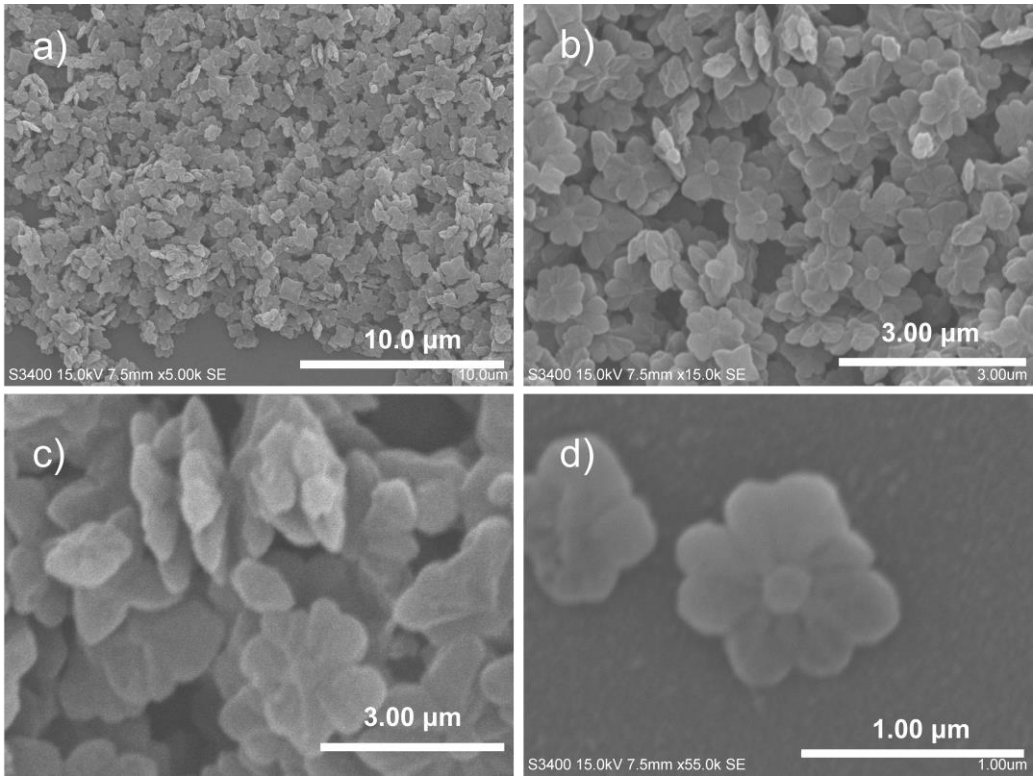

Figure S21. SEM of Ni4TQ assemblies obtained from MeOH:THF = 8:2 with final concentration of ~5 µM.

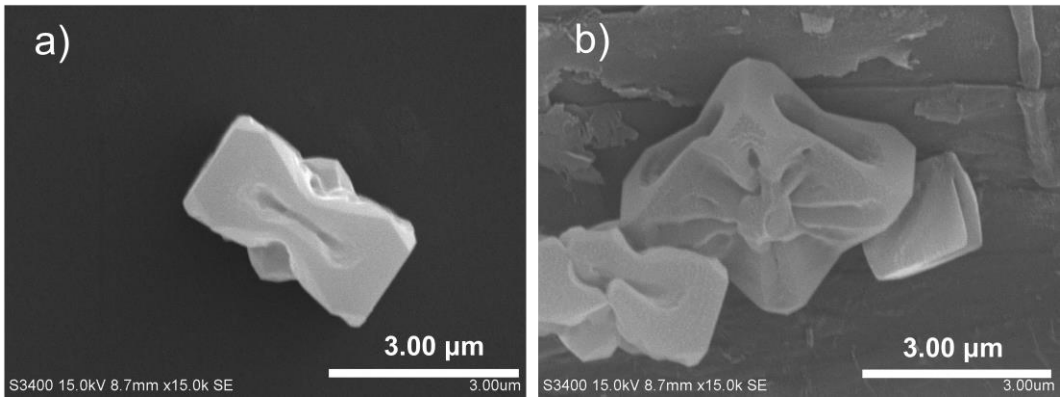

Figure S22. SEM of Ni4TQ assemblies obtained from MeOH:THF = 7:3 after 1 hour with final concentration of ~5 µM.

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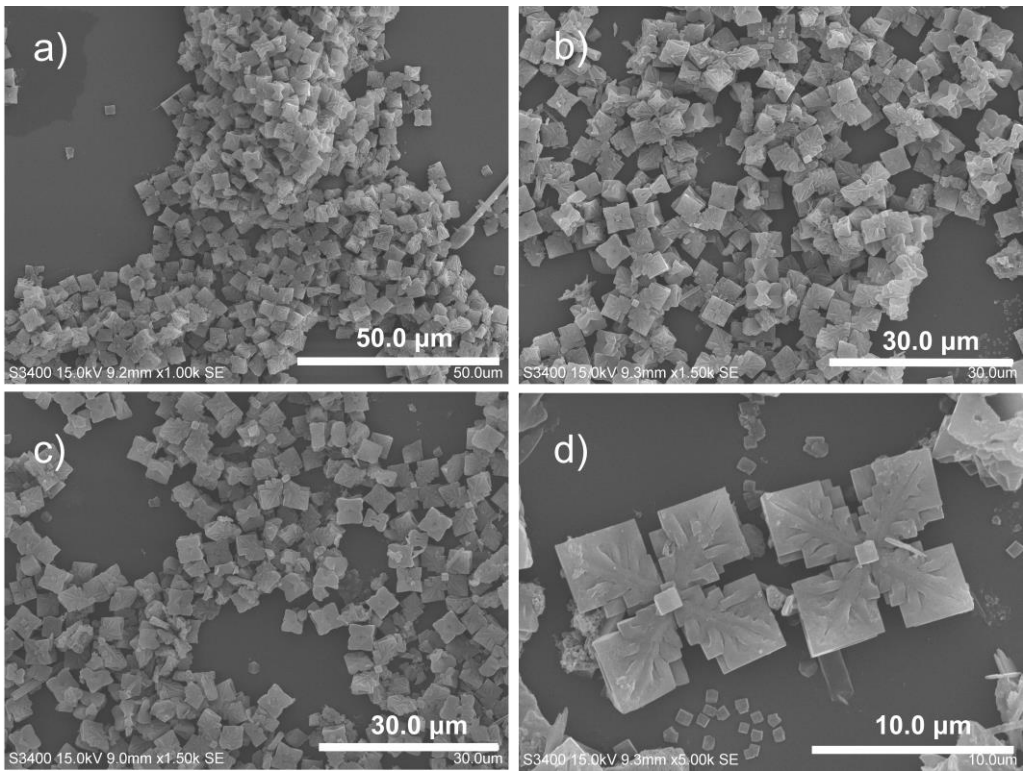

Figure S23. SEM of Ni4TQ assemblies obtained from MeOH:THF = 7:3 with elongation of aggregation time to 18 hours at final concentration of ~5 µM.

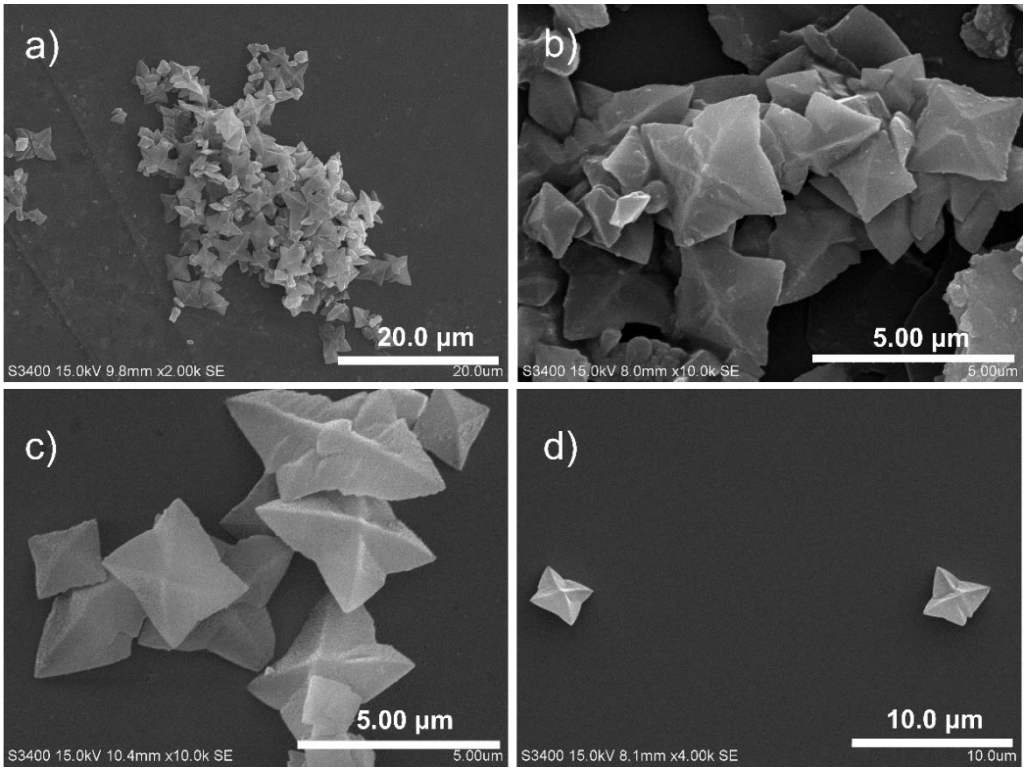

Figure S24. SEM of Ni4TQ assemblies obtained from isopropanol:THF = 100:1 (d) with final concentration of ~5 µM.

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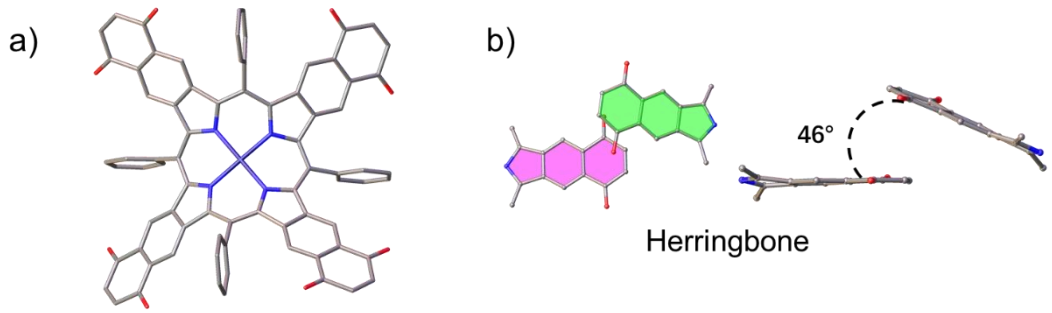

Figure S25. (a) Crystal structure of Ni4NQ (tert-butyl group are omitted for clarity) and (b) partial crystal packing of Ni4NQ. The crystal data is obtained from reference [3].

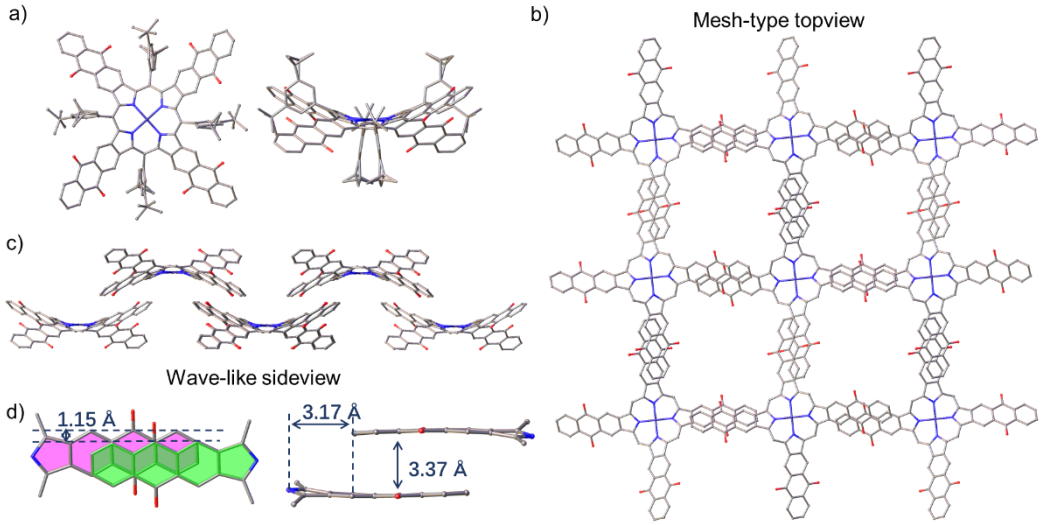

Figure S26. (a) Crystal structure (hydrogens are omitted for clarity) and (b-d) crystal packing (hydrogens and the *meso*-substituents are omitted for clarity) of Ni4AQ.

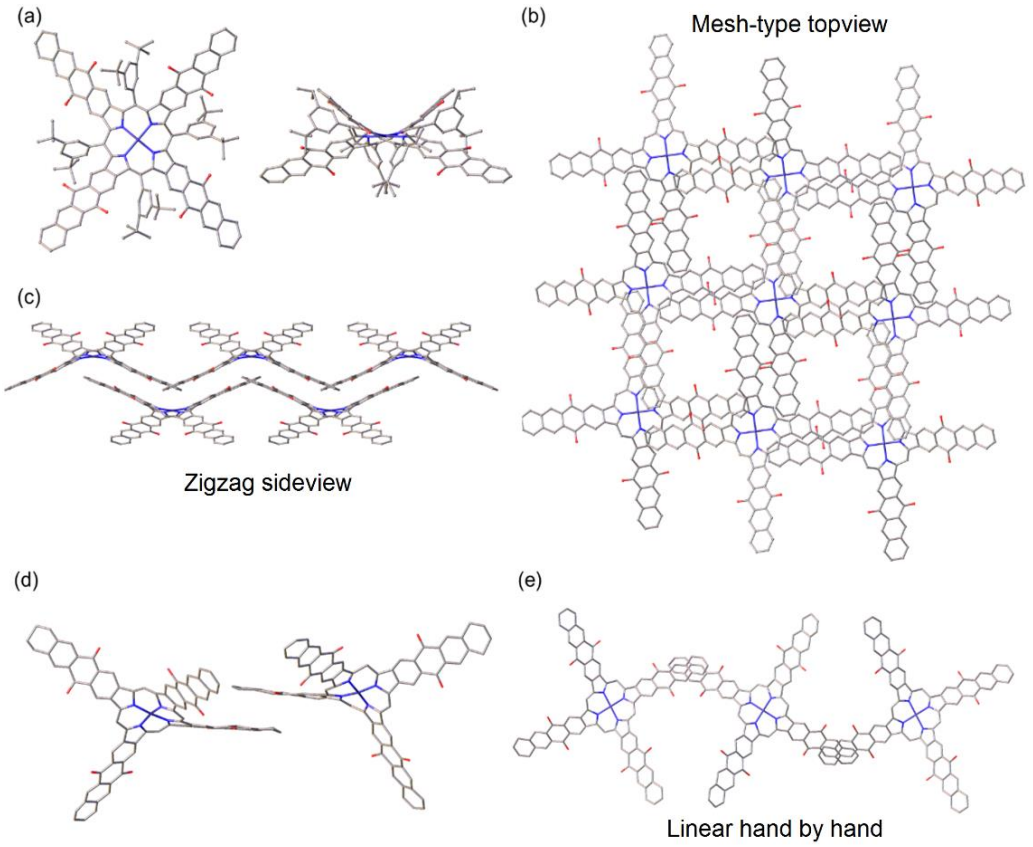

Figure S27. (a) Crystal structure (hydrogens are omitted for clarity), (b-c) crystal packing (hydrogens and the *meso*-substituents are omitted for clarity) obtained from the crystal grown from toluene/*n*-hexane; and (d-e) crystal packing (hydrogens and the *meso*-substituents are omitted for clarity) obtained from rough crystal grown from CS_2/*n*-hexane of Ni4TQ.

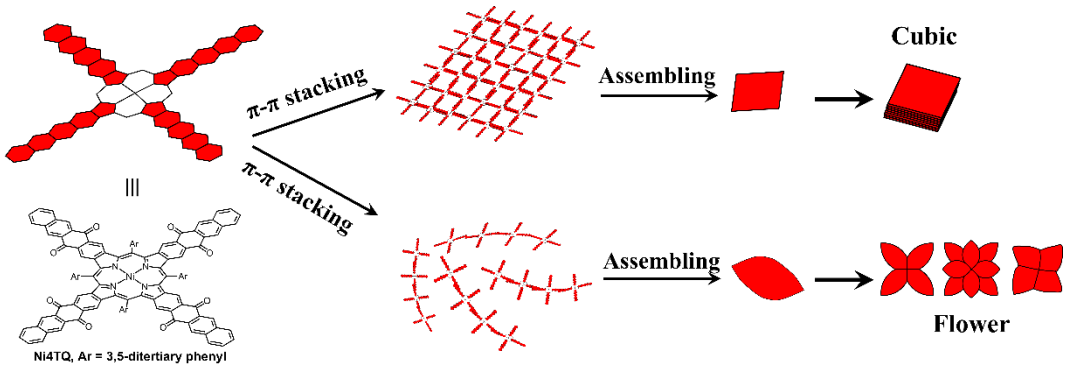

Figure S28. The proposed relationship between the molecular packing and the resulted morphs.

Table S2. Crystal Data and Structure Refinements of Ni4TQ and Ni4AQ.

Compounds	**Ni4TQ**	**Ni4AQ**
Formula	$C_{140.6}H_{117.831}N_4NiO_8$	$C_{124}H_{108}N_4NiO_8$
Formula weight (g/mol)	2045.79	1840.85
crystal system	Tetragonal	Tetragonal
Temperature (K)	100	295 K
Crystal size (mm)	0.2 × 0.2 × 0.15	0.23 × 0.18 × 0.1
Theta range for data collection (°)	3.00-67.94	4.51-67.89
space group	*P*4	*P*42/*n*
a (Å)	20.4751(3)	22.271(2)
b (Å)	20.4751(3)	22.271(2)
c (Å)	13.4593(10)	12.5290(16)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Volume ($Å^3$)	5642.5(5)	6214.2 (15)
Z	2	2
ρ_{calc} (g/cm^3)	1.204	0.984
F (000)	2158	1944
μ (mm–1)	0.73	0.62
Index ranges	-24 ⩽ h ⩽ 18 -24 ⩽ k ⩽ 15 -16 ⩽ l ⩽ 16	-23 ⩽ h ⩽ 26 -27 ⩽ k ⩽ 20 -14 ⩽ l ⩽ 14
*R*1 [I > 2σ(I)]	0.071	0.097
*wR*2 (all data)	0.221	0.311
GOF	1.059	1.189
Reflections collected/Unique	23848	48412
CCDC number	2082681	2082682

5. References

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[2] Tilley, A. J.; Pensack, R. D.; Kynaston, E. L.; Scholes, G. D.; Seferos, D. S. Singlet Fission in Core-Shell Micelles of End-Functionalized Polymers. *Chem. Mater*. **2018**, *30*, 4409-4421.

[3] Banala, S.; Wurst, K.; Kräutler, B. Panchromatic-Extended Porphyrins from Conjugation with Quinones. *ChemPlusChem* **2016**, *81*, 477-488.

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