Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Discrete and Dispersible Metalloporphyrin-Based CMP Nanoparticles Enabling Colorimetric Detection and Quantitation of Gaseous SO_2

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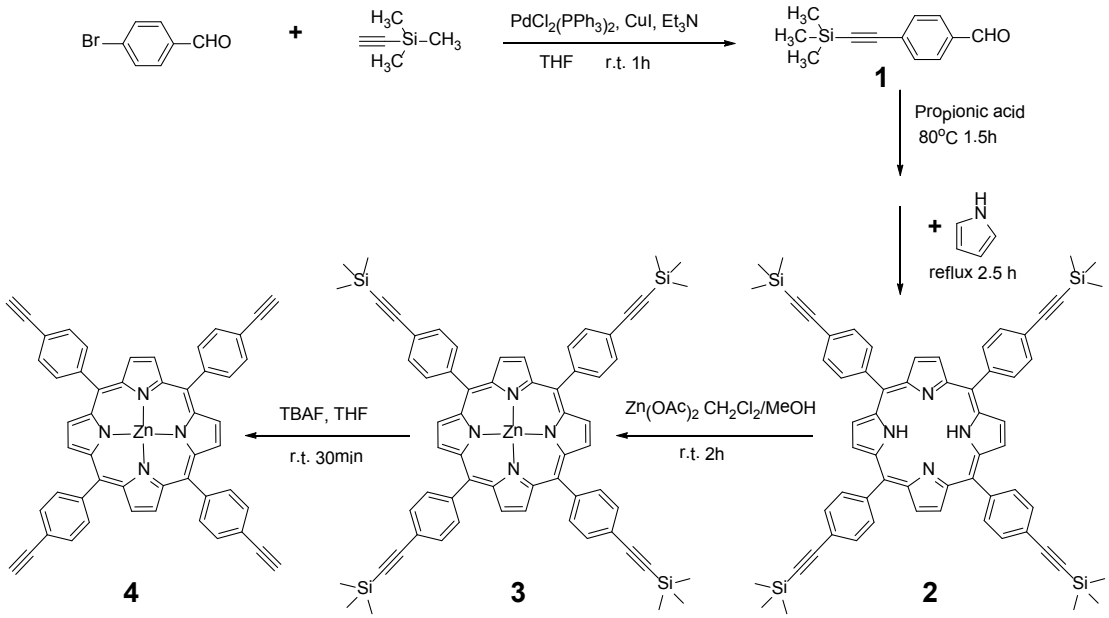
Section 1. Materials and Methods

1.1 Materials and Methods

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Double-distilled water was used throughout the experiments. THF was freshly distilled from K/benzophenone ketyl under nitrogen. Copper iodide and tetrabutylammonium fluoride (TBAF) were purchased from Adamas (Swiss). Trimethylsilylacetylene, bis(triphenylphosphine)palladium(II) dichloride were purchased from Energy (China). Pyrrole, pyrrolidine were purchased from Aladdin (China).

1.2 Synthesis of Zn-Por monomer



4-(trimethylsilylethinyl)benzaldehyde (1) [S1, S2]

To a stirred mixture of 9.25 g (50.0 mmol) of 4-bromobenzaldehyde, 381 mg (2.0 mmol) of CuI, and 702 mg (1.0 mmol) of $Pd(PPh_3)_2Cl_2$ in 70 ml of THF was added 7.59 g (75 mmol) of triethylamine. A solution of trimethylsilylacetylene (7.97 ml, 56 mmol) in 18 ml of THF was then added (very slowly) over 1.5 h. The solvent was evaporated, and the residue was treated by pentane. Filtration through Celite and evaporation of the solvent under vacuum to give a thick oil, which was immediately purified by column

chromatography (eluent: n-hexane/CH_2Cl_2= 3 : 2) afforded 4-(trimethylsilylethinyl)-benzaldehyde (9.27 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.27 (Si-CH_3, s, 9 H), 7.60 (m-ArH, d, J = 8.4 Hz, 2 H), 7.81 (o-ArH, d, J = 8.4 Hz, 2 H), 10.00 (-CHO, s, 1 H).

5,10,15,20-Tetrakis-(4-[(trimethylsilyl)ethynyl]phenyl)porphyrin (2) [S3, S4]

A solution of 4-(trimethylsilylethynyl)benzaldehyde (**1**, 8.09 g, 40 mmol) in propionic acid (160 ml) was stirred in a 250 ml three-neck flask for 1.5h at 80 °C. While shielding from the light, Pyrrole (2.80 ml, 40.4 mmol) was added and the resulting solution heated under reflux for 2.5 h, after which it was allowed to cool to room temperature. A black solid precipitated and the suspension was allowed to settle overnight. The black liquid was removed by filtration and the remaining black solid was washed with methanol until the filtrate was colorless. The residue was purified through column chromatography (eluent: n-hexane/$CHCl_3$, from 3 : 1 to 0 : 1) to produce a purple powder (3.33 g, 33%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) −2.84 (NH, s, 2 H), 0.38 (Si-CH_3, s, 36 H), 7.86 (m-ArH, d, J = 7.80 Hz, 8 H), 8.13 (o-ArH, d, J = 7.80 Hz, 8 H), 8.82 (Pyrrole-H, s, 8 H). UV–Vis ($CHCl_3$): λmax/nm: 422.5; 517.5; 553.0; 591.5; 648.5.

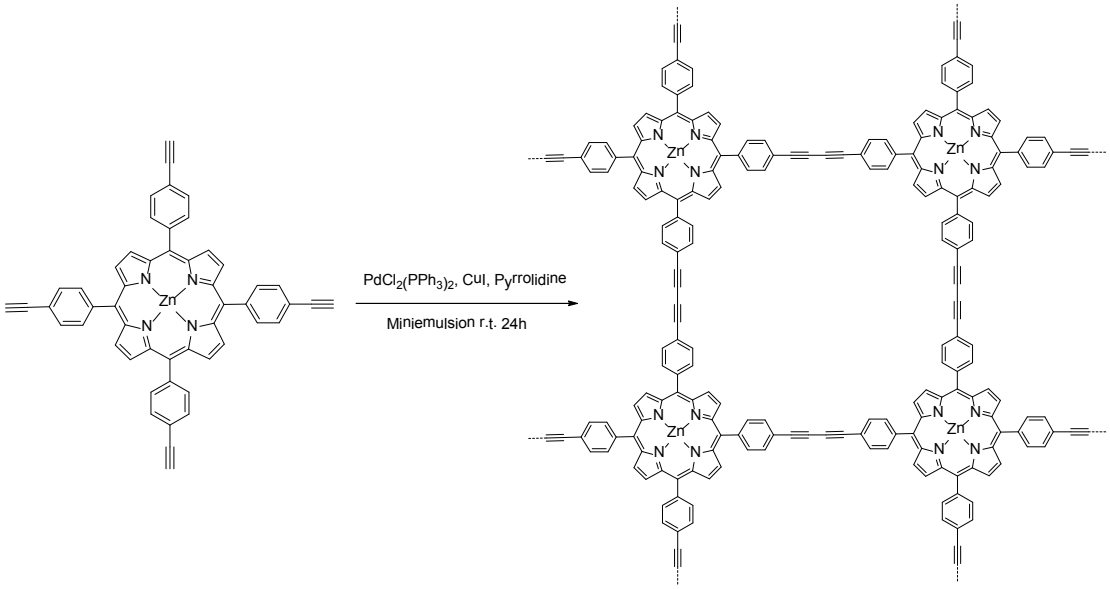
5,10,15,20-Tetrakis-(4-[(trimethylsilyl)ethynyl]phenyl)porphyrin-zinc(II) (3) [S5]

5,10,15,20-tetrakis-(4-[(trimethylsilyl)ethynyl]phenyl)porphyrin (**2**, 1.37 g, 1.37 mmol) was dissolved in CH_2Cl_2 (ca. 850 mL) and a solution of $Zn(OAc)_2$ (5.03 g, 2.74 mmol, 20 eq,) in MeOH (ca. 85 mL) was added. After 2h stirring at room temperature, the solvent was evaporated and the remaining solid was dissolved in $CHCl_3$ (3 mL) and eluted through a silica column. Since the impurities were wiped off with n-hexane/CH_2Cl_2 = 1 : 2 as eluent, the aubergine product was eluted by ample $CHCl_3$ (1.04 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.38 (Si-CH_3, s, 36 H), 7.86 (m-ArH, d, J = 7.50 Hz, 8 H); 8.13 (o-ArH, d, J = 7.20 Hz, 8 H); 8.91 (Pyrrole-H, s, 8 H). UV–Vis ($CHCl_3$): λmax/nm: 423.5; 549.0; 587.5. MALDI-TOF (m/z): 1062.32 (calc. 1062.91).

5,10,15,20-Tetrakis-(4-(ethynyl)phenyl)porphyrin-zinc(II) (4) [S5]

TBAF (1 M in THF, 3.75 mL, 3.75 mmol) was added to a solution of (5,10,15,20-tetrakis-(4-ethynylphenyl)porphyrin-Zn(II) (797 mg, 0.75 mmol) in dry THF (ca. 75 mL). After stirring at room temperature for 30 min, the reaction was quenched with water and a purple solid precipitated. The solvent was removed by filtration, yielding the purple end-product (575 mg, 99%). ^{1}H NMR (400 MHz, $(CD3)_2SO$): δ (ppm) 4.47 (acetylene H, s, 4 H); 7.89 (m-ArH, d, J = 7.80 Hz, 8 H); 8.17 (o-ArH, d, J = 8.10 Hz, 8 H); 8.80 (Pyrrole-H, s, 8 H). UV–Vis ($CHCl_3$): λmax/nm (logε): 422.0; 548.0; 586.5. MALDI-TOF (m/z): 772.41 (calc. 772.16). Elemental analysis calcd (%) for $C_{52}H_{28}N_4Zn$: C, 80.67; H, 3.65; N, 7.24; Zn, 8.45. Found: C, 80.46; H, 3.80; N, 7.06; Zn, 8.68.

1.3 Synthesis of Zn-Por NCMPs and bulky CMP [S6,S7]



Zn-Por NCMPs

5,10,15,20-Tetrakis-(4-(ethynyl)phenyl)porphyrin-zinc(II) (77.4 mg, 0.1 mmol), Bis-(triphenylphosphine)palladium(II) dichloride (7 mg, 0.01 mmol), and copper iodide (1.9 mg, 0.01 mmol) were dispersed in the mixture of toluene (2 mL) and pyrrolidine (2 mL), and the solution was stirred until the solid dissolved completely. The deep purple solution obtained was mixed with 20 mL of a 1% aqueous cetyltrimethyl ammonium

bromide (CTAB) solution. After ultrosonicated for 20 min (SONICS-750 with a tip operated at 75 W), the forming miniemulsion was stirred for 24 h at room temperature without any heating. The product was obtained by precipitation in ethanol and thoroughly washed with THF to remove the surfactants and any unreacted monomer or catalyst residues. As the solvent THF was replaced by dioxane, the dried redispersible nanoscale CMPs were obtained via freeze-drying method. (Yield, 82%).

Bulky Zn-Por CMPs

5,10,15,20-Tetrakis-(4-(ethynyl)phenyl)porphyrin-zinc(II) (77.4 mg, 0.1 mmol), Bis-(triphenylphosphine)palladium(II) dichloride (7 mg, 0.01 mmol), and copper iodide (1.9 mg, 0.01 mmol) were dissolved in a mixture of toluene (2 mL), and pyrrolidine (2 mL) was added and stirred until the solid was dissolved completely. The deep purple solution was stirred for 24 h at room temperature without any heating and gradually turned into dark green. The resulting precipitate was collected by centrifugation, thoroughly washed with THF and dioxane to remove the surfactants and any unreacted monomer or catalyst residues, and dried via freeze-drying method to give Zn-Por bulky CMPs in 98%. The pore parameters of bulky CMPs measured by N_2 adsorption at 77K were estimated to show a specific surface area of 210.2 m^2/g, a pore volume of 0.3555 cm^3/g, and a pore size range from 1.3 to 5 nm.

1.4 Characterization

UV-Vis spectra were recorded on a Shimadzu UV-3600 PC spectrometer (Shimadzu Japan). For tracking the reliable absorbance change, we prepared the freshly saturated solution of SO_2 in $CHCl_3$ (2.5 mM) and added it stepwise into the NCMP solution for the colorimetric detection. The displacement reaction proceeded for 10 min to allow the system to equilibrate, and then the detection was performed at least three times on the UV-vis spectrometry, ensuring the results acquired at the steady state. ^{1}H NMR spectra were recorded on a Bruker DRX 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) as the internal standard (Bruker Germany). Matrix Assisted Laser Desorption/ Ionization-Time of Flight Mass

(MALDI-TOF MS) spectra were performed on a Voyager-DE-STR spectrometer in reflector mode using dithranol as a matrix (Applied Biosystems USA). Solid-state ^{13}C CP/MAS NMR measurements were performed on a Bruker 400 MHz NMR spectrometer at a MAS rate of 12 kHz and a CP contact time of 2 ms (Bruker Germany). Elemental analyses were carried out on a varioEL3 analyzer (Elementar Germany). HR TEM was carried on a JEM-2010 transmission electron microscope at an acceleration voltage of 200 kV (JEOL, Japan). The sample was prepared by drop-casting a sonicated THF dispersion onto a copper grid. TGA measurements were carried out on a Pyris 1 TGA by heating the sample from 100 °C at a heating rate of 20 °C min^{-1} (Perkin Elmer, USA). Nitrogen sorption measurements were collected at 77 K by an ASAP2020 volumetric adsorption analyzer (Micromeritics, USA). The samples were degassed at 130 °C for more than 12 h before measurement. The hydrodynamic diameter of the NCMPs was achieved using a Zetasizer Nano at 25 °C (Malvern, UK).

References

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[S6] I. J. S. Fairlamb, P. S. Bauerlein, L. R. Marrison and J. M. Dickinson, *Chem. Commun.*, 2003, 632.

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Section 2. TEM image of bulky CMPs

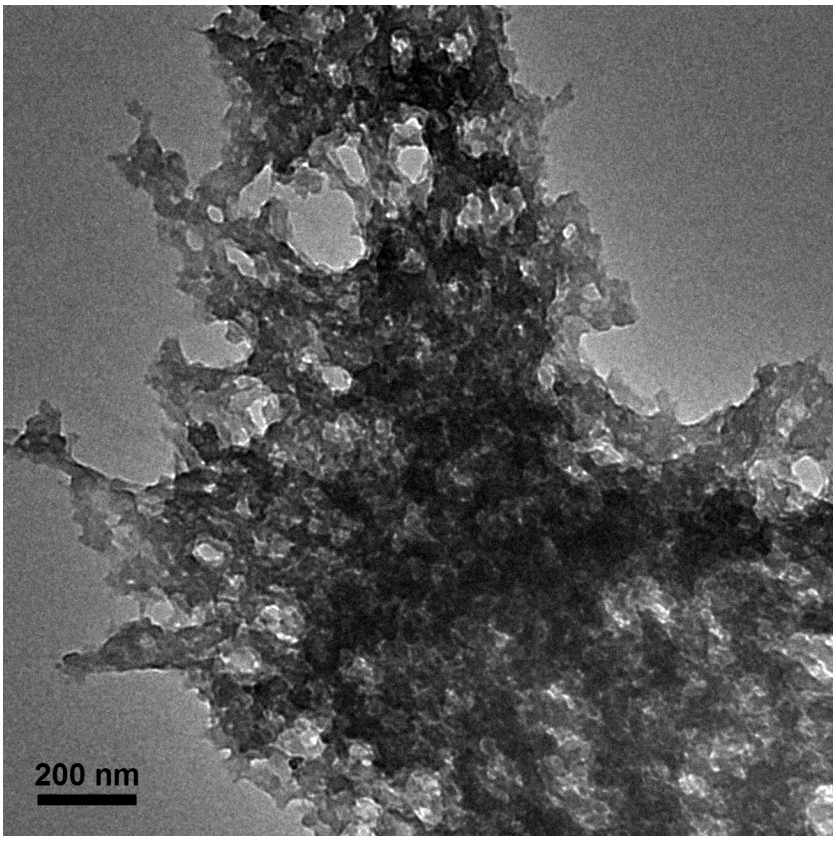


Fig. S1 TEM image of the bulky Zn-Por CMPs

Section 3. Thermo gravimetric analysis.

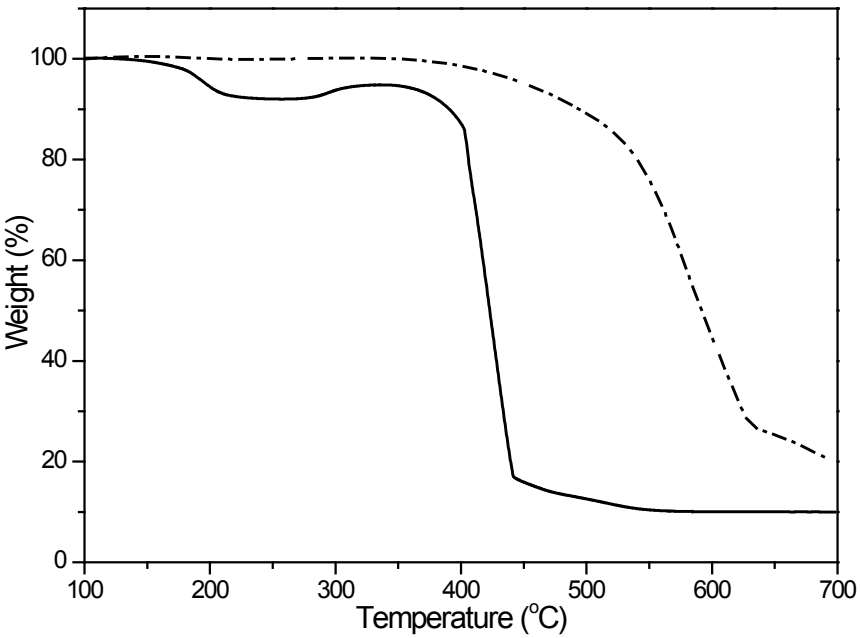
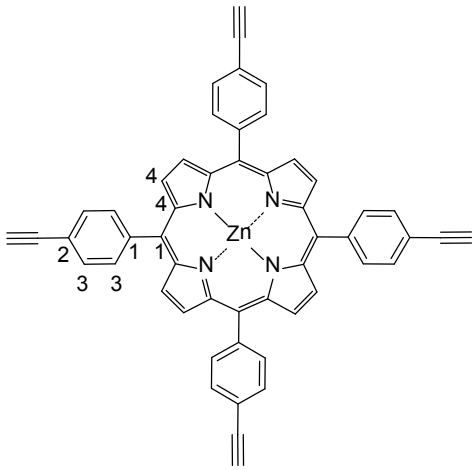


Fig. S2 TGA curves of Zn-Por monomer (solid line) and Zn-Por NCMP (dash dotted line) measured in air.

Section 4. Solid-state ^{13}C NMR spectrum



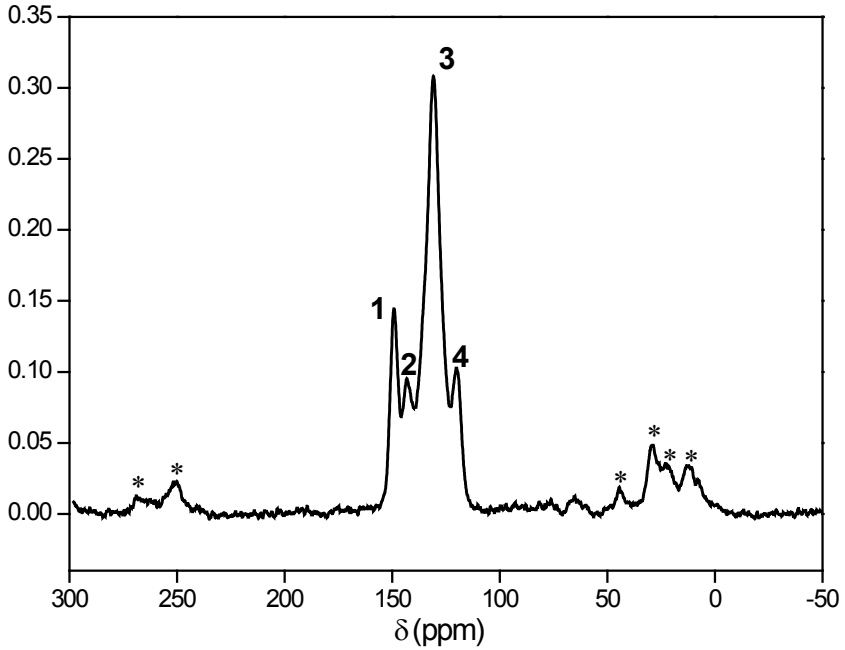


Fig. S3 Solid-state ^{13}C CP/MAS NMR spectra of Zn-Por NCMPs at a CP contact time of 2 ms and a MAS rate of 12 kHz. Signals with * symbols are side peaks.

Section 5. Color change of Zn-Por solution in detection of SO_2 and their stability testing

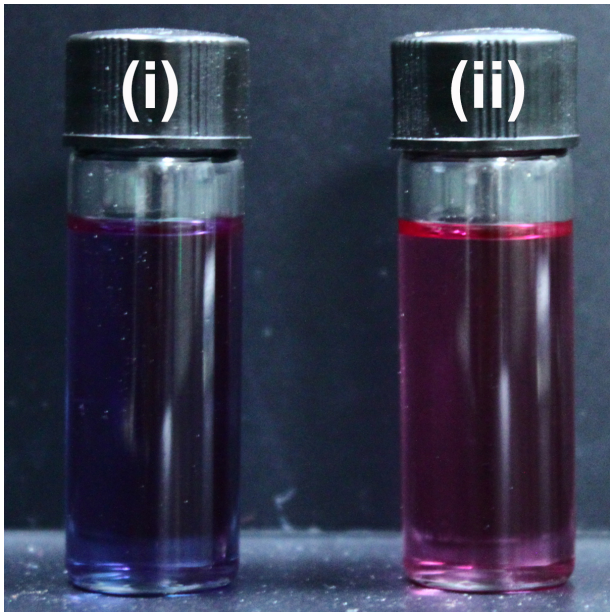


Fig. S4 The color change of Zn-Por solution in $CHCl_3$ before (i) and after (ii) bubbling SO_2.

Fig. S5 The color change of Zn-Por solution in $CHCl_3$ before (i) and after (ii) addition of pyrrolidine, and the solution (ii) standing for 3 days (iii).

Section 6. SO_2 detection using bulky Zn-Por CMPs

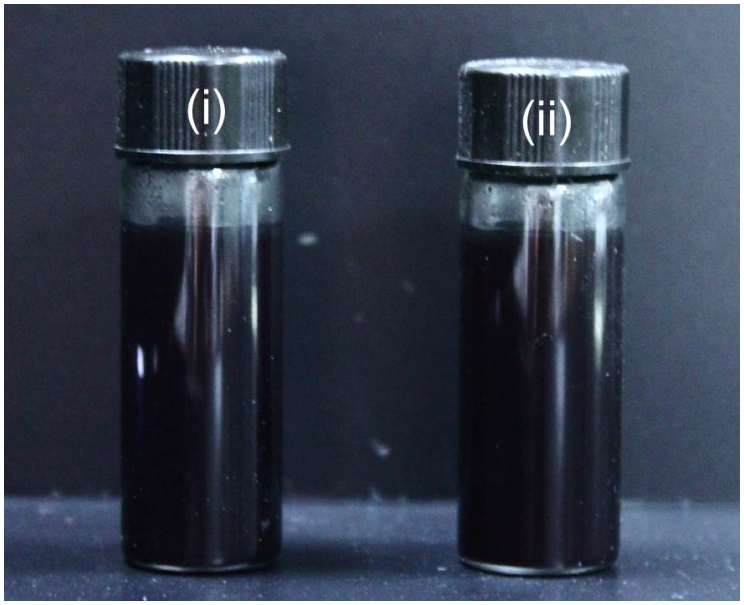


Fig. S6 The suspension of bulky Zn-Por CMPs in $CHCl_3$ before (i) and after (ii) bubbling SO_2.

Fig. S7 SO_2 test paper made by the suspension of pyrrolidine•CMP complexes as exposed to air (i) and SO_2 (ii) atmospheres, respectively.