Microwave-assisted synthesis of a viologen-based covalent organic polymer with redox-tunable polarity for dye adsorption

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General materials and methods.

All reagents and starting materials were purchased from Sigma-Aldrich and used without further purification. Syntheses of precursors 1,1’-bis(2,4-dinitrophenyl)dichloride4,4’-bipyridinium, (DNP-BP), hexakis(4-chloromethylphenoxy)cyclotriphosphazene (P1) were accomplished according to the literature\textsuperscript{1,2,3} with slight modifications and are reported in the synthesis section. Deionized water was used from Millipore Gradient Milli-Q water purification system. Thin-layer chromatography (TLC) was performed on silica gel 60 F254 (E. Merck). The plates were inspected with UV light. Column chromatography was performed on silica gel 60F (Merck 9385, 0.040–0.063 mm). Routine nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on a Bruker Avance spectrometer, with working frequency of 600 and 500 MHz for \textsuperscript{1}H, and 151.0 MHz for \textsuperscript{13}C nuclei, respectively. All chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents (CD\textsubscript{3}CN: δ = 1.94 ppm, CD\textsubscript{3}OD: δ = 3.31 ppm, D\textsubscript{2}O: δ = 4.97 ppm and DMSO-d\textsubscript{6}: δ = 2.50 ppm). Coupling constant values (J) are given in hertz (Hz), the multiplicity is abbreviated in the following way: s (singlet) and d (doublet). FTIR studies were carried out on Agilent 670-IR spectrometer. TGA experiments were performed on TA SDT Q600. SEM images were obtained from FEI Quanta 450FEG. UV-Vis studies were carried out on Cary 5000 UV-Vis-NIR spectrophotometer. All UV-Vis spectra were recorded at room temperature of 298 K in a quartz cell with 10 mm path length. Solid-state crosspolarization magic angle spinning (CP/MAS) \textsuperscript{13}C and \textsuperscript{31}P NMR spectra of polymer samples were recorded on a Bruker Avance III 400 WB (400 MHz) NMR spectrometer at ambient temperature with a magic angle spinning rate of 7.0 kHz. Raman measurements were performed with a Witec Alpha 300 confocal Raman system. The samples were illuminated with a 532 nm laser and an acquisition times between 25 and 80 s. CO\textsubscript{2} and N\textsubscript{2} adsorption/desorption isothermal curves were recorded both at 273 K and 298 K and up to 1 bar using a manometric Micromeritics 3Flex gas sorption analyzer along with a PolyScience Circulating bath (50:50 vol% water:ethylene glycol mixture) for maintaining constant temperature during experiment.
Synthesis. Detailed syntheses of all the precursor were reported in our paper Das, G., Prakasam, T., Nuryyeva, S., Han, D.S., Abdel-Wahab, A., Olsen, J.C., Polychronopoulou, K., Platas-Iglesias, C., Ravaux, F., Jouiad, M. and Trabolsi, A., *J. Mater. Chem. A*, 2016, 40, 15361-15369.

Scheme S1. Synthesis of COP$_{1}^{++}$ from the phosphonitrilic chloride trimer, P$_{1}$, and 4-hydroxybenzaldehyde.
**FTIR.** The formation COP$_1^{++}$ was confirmed by FTIR using an Agilent Technologies Cary 600 Series FTIR Spectrometer. Figure S1 shows the characteristic absorption bands of COP$_1^{++}$, COP$_1^{+}$, COP$_1^{0}$ and starting materials P1 and dipyridyl.

![Figure S1](image)

**Figure S1.** Stacked FTIR spectra of the three redox states of the COP$_1$ polymer, COP$_1^{++}$, COP$_1^{+}$ and COP$_1^{0}$, and the two precursor molecules, 4,4'-bipyridine and hexakis(4-chloromethylphenoxy)cyclotriphosphazene, P1.

**Solid state NMR.**
Figure S2. CP/MAS $^{13}$C NMR spectrum of COP$_1^{++}$ with peak assignments.

Figure S3. $^{31}$P NMR spectrum of COP$_1^{++}$.

TGA.

Figure S4. TGA profile for COP$_1^{++}$. 
Figure S5. TGA profile for COP$_1$$^+$.

93.8% at 175.7 °C

Figure S6. TGA profile for COP$_1$$^0$.

89.1% at 380.3 °C
**PXRD.** The amorphous character of polymers were determined by PXRD.

![PXRD Patterns](image)

**Figure S7.** PXRD patterns of COP\(^{1+}\) (black), COP\(^{1+}\) (red) and COP\(^{0}\) (blue).

Nitrogen and CO\(_2\) gas adsorption.

![Nitrogen and CO\(_2\) Adsorption](image)

**Figure S8.** a) N\(_2\) adsorption isotherm of COP\(^{1+}\) at room temperature and b) CO\(_2\) adsorption isotherm of COP\(^{1+}\) at room temperature.
Solid state EPR.

Figure S9. Solid-state EPR spectra of COP$_1^{++}$ (a), COP$_1^-$ (b) and COP$_1^0$ (c).

Solid State UV-Vis.

Figure S10. Solid-state UV spectra of COP$_1^{++}$ and COP$_1^-$.

Dyes release. Fluorescein was removed from the polymer by immersion in a saturated solution of NaCl. Nile red was removed by washing the adsorbed polymer in methanol (a spectrofluorometric method).
Figure S11. UV-Vis spectra of fluorescein dye at different time released from COP$_1^{++}$. Spectra were recorded at room temperature.

Figure S12. Fluorescence spectra of Nile red dye released over time from the COP$_1^0$. Spectra were recorded in methanol at room temperature.
Figure S13. Release of Nile red from COP$_1^0$ over time

Characterization after dye removal: FTIR.

Figure S14. FT-IR spectra of COP$_1^{++}$ before (blue) and after (green) dye removal.
Characterization after dye removal: SEM.

Figure S15. SEM images of COP$_{1}^{++}$ before (a) and after (b) dye removal.