Multi-Stimulus Responsive Polyoxometalate-Viologen Hybrid Ionic Liquids for Rewritable Inkless Printing and Environmental Monitoring

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(1) $C_3BPY \cdot Br$

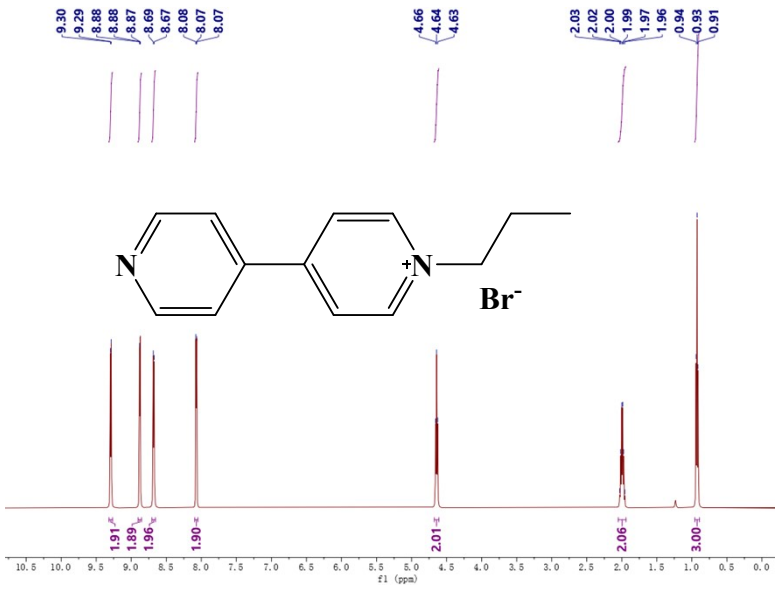


Fig. S1. ^1H NMR of $C_3BPY \cdot Br$.

^1H NMR (500 MHz, DMSO-d_6), δ ppm: 9.29 (d, J = 6.4 Hz, 2H), 8.90 – 8.85 (m, 2H), 8.68 (d, J = 6.3 Hz, 2H), 8.10 – 8.05 (m, 2H), 4.64 (t, J = 7.3 Hz, 2H), 1.99 (h, J = 7.3 Hz, 2H), 0.93 (t, J = 7.3 Hz, 3H).

(2) $C_4BPY \cdot Br$

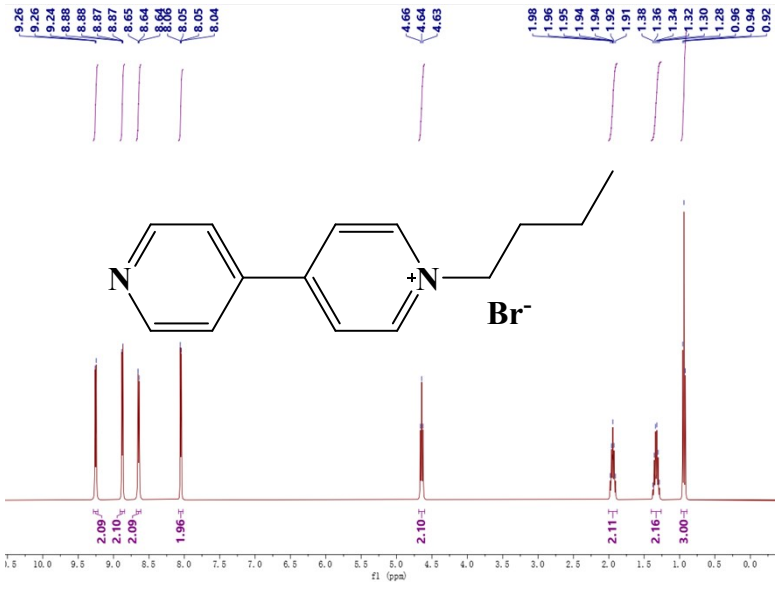


Fig. S2. ^{1}H NMR of C_4BPY·Br.

^{1}H NMR (500 MHz, DMSO-d_6), δ ppm: 9.28 – 9.22 (m, 2H), 8.91 – 8.84 (m, 2H), 8.65 (d, J = 6.7 Hz, 2H), 8.08 – 8.02 (m, 2H), 4.64 (t, J = 7.4 Hz, 2H), 1.94 (p, J = 7.5 Hz, 2H), 1.33 (h, J = 7.4 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H).

(3) C_5BPY·Br

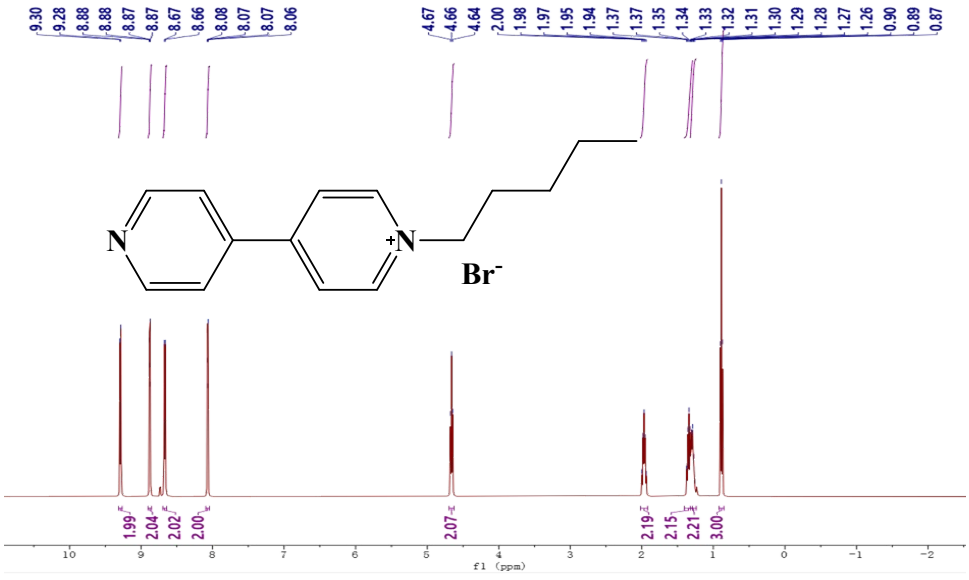


Fig. S3. ^{1}H NMR of C_5BPY·Br.

^{1}H NMR (500 MHz, DMSO-d_6), δ ppm: 9.29 (d, J = 6.5 Hz, 2H), 8.90 – 8.85 (m, 2H), 8.67 (d, J = 6.5 Hz, 2H), 8.09 – 8.04 (m, 2H), 4.66 (t, J = 7.4 Hz, 2H), 1.97 (p, J = 7.5 Hz, 2H), 1.40 – 1.29 (m, 2H), 1.29 (dd, J = 10.4, 5.5 Hz, 2H), 0.89 (t, J = 7.0 Hz, 3H).

(4) C_6BPY·Br

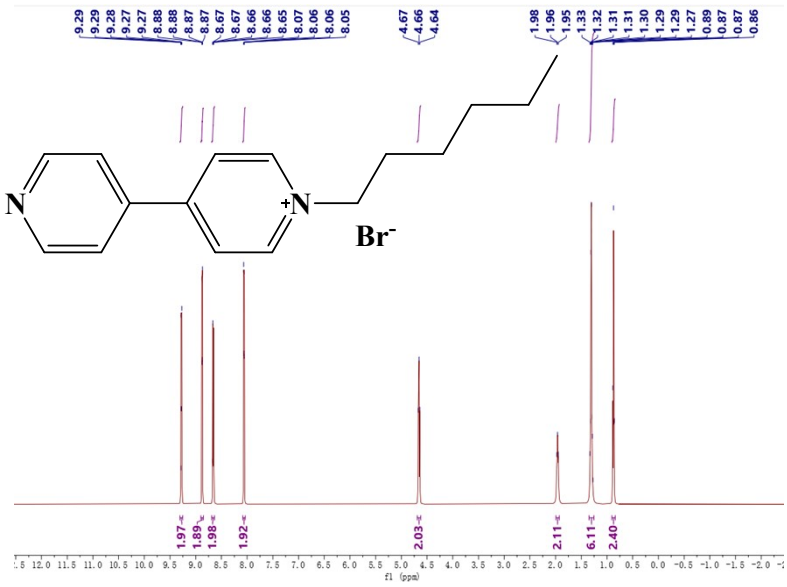


Fig. S4. ^{1}H NMR of C_6BPY·Br.

^{1}H NMR (500 MHz, DMSO-d_6), δ ppm: 9.31 – 9.25 (m, 2H), 8.90 – 8.85 (m, 2H), 8.69 – 8.63 (m, 2H), 8.09 – 8.04 (m, 2H), 4.66 (t, J = 7.5 Hz, 2H), 1.96 (t, J = 7.2 Hz, 2H), 1.30 (q, J = 8.6, 4.3, 3.7 Hz, 6H), 0.90 – 0.84 (m, 2H).

(5) C_{12}BPY·Br

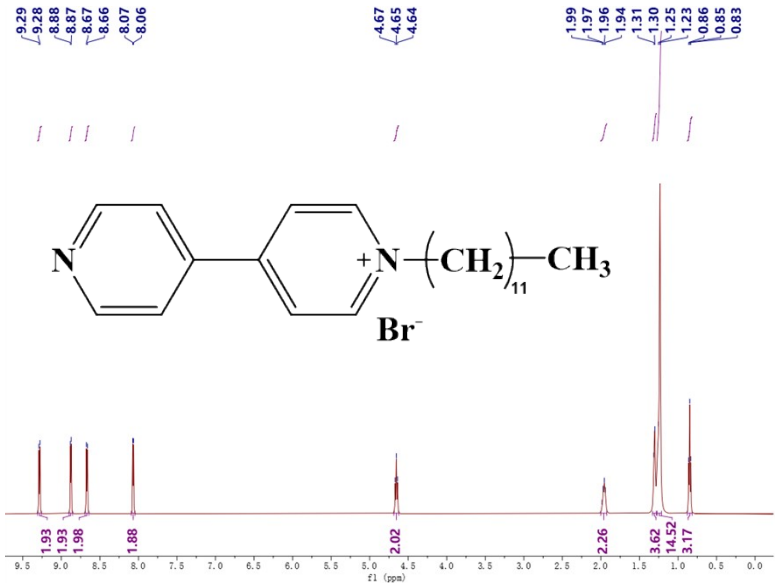


Fig. S5. ^{1}H NMR of C_{12}BPY·Br.

^{1}H NMR (500 MHz, DMSO-d_6), δ ppm: 9.28 (d, J = 6.3 Hz, 2H), 8.88 (d, J = 5.1 Hz, 2H), 8.67 (d, J = 6.2 Hz, 2H), 8.07 (d, J = 5.2 Hz, 2H), 4.65 (t, J = 7.4 Hz, 2H), 1.96 (q, J = 7.3 Hz, 2H), 1.31 (d, J = 6.0 Hz, 4H), 1.24 (d, J = 10.2 Hz, 15H), 0.85 (t, J = 6.7 Hz, 3H).

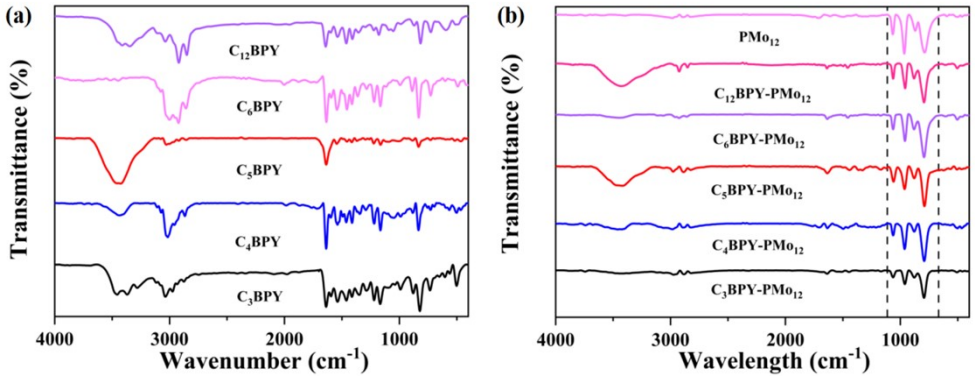
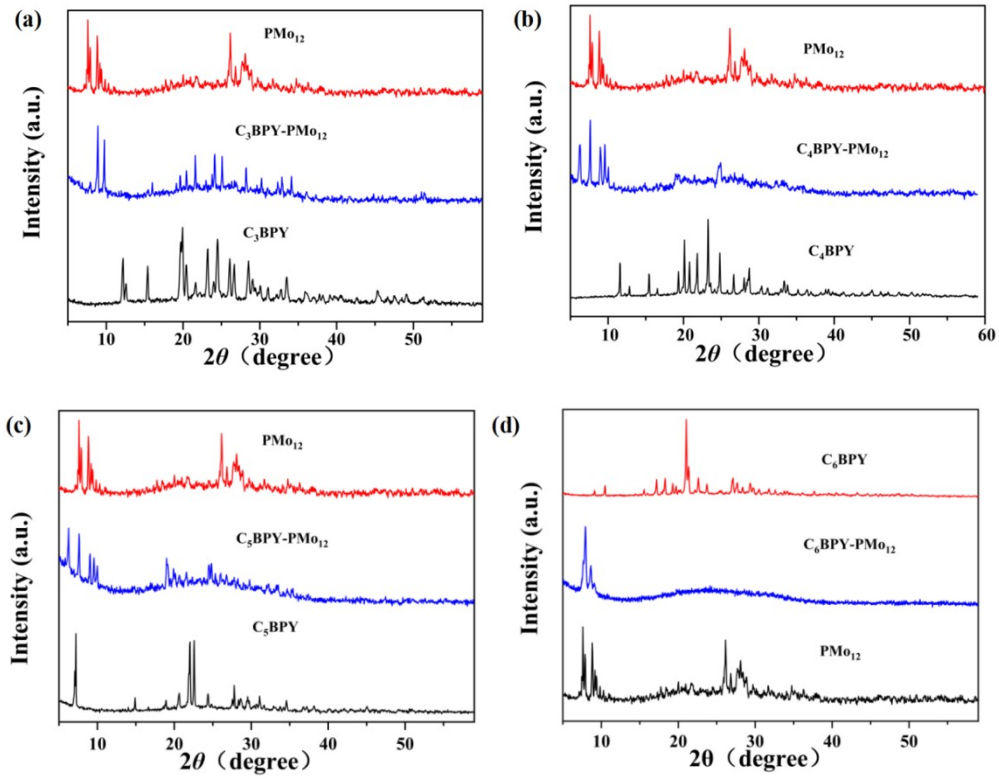


Fig. S6. The FT-IR spectra of $C_n$bpy (a) and C_n-PMo_{12} (b).



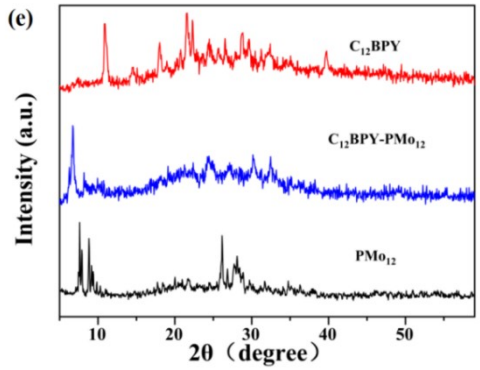
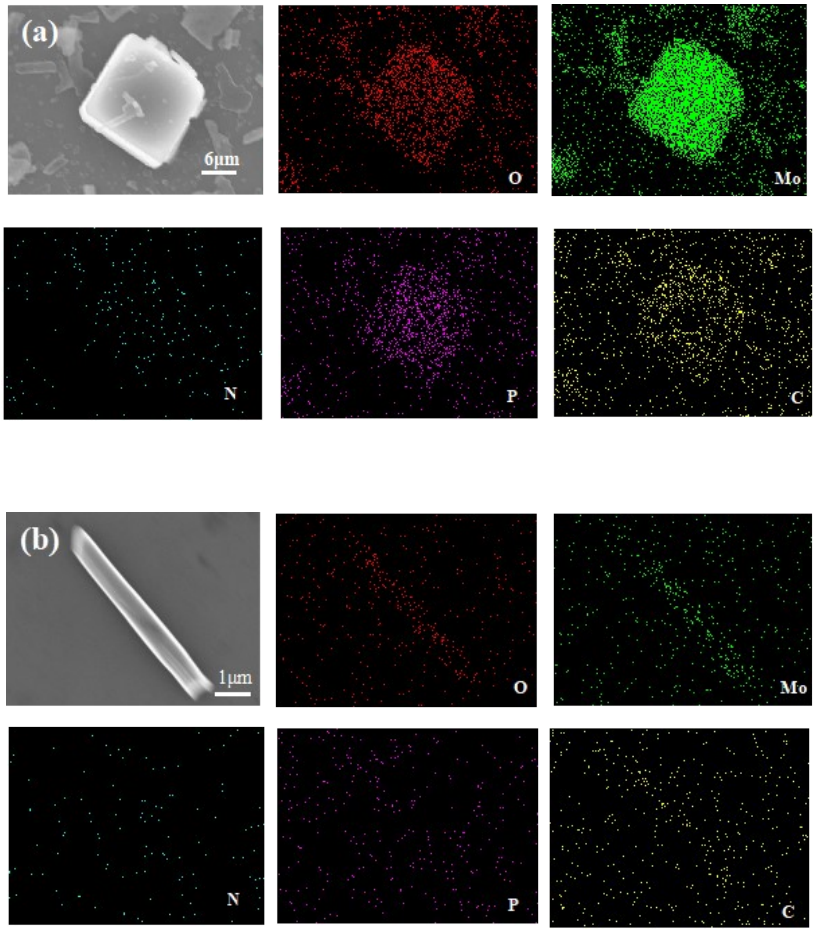


Fig. S7. (a-e) The XRD spectra of (a) C_3-PMo_{12}, (b) C_4-PMo_{12}, (c) C_5-PMo_{12}, (d) C_6-PMo_{12}, (e) C_{12}-PMo_{12}.



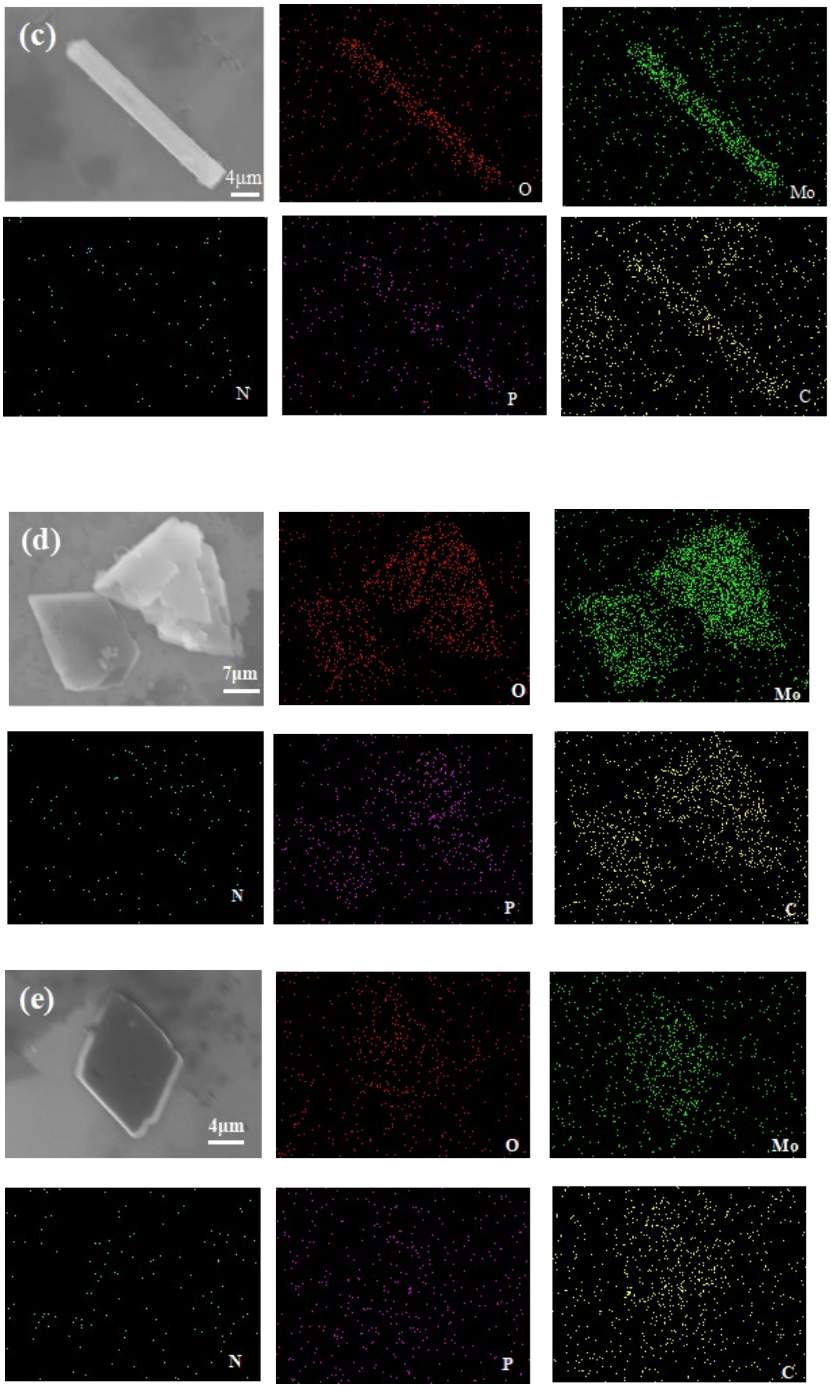


Fig. S8. (a-e) The elemental mapping of O, N, Mo, C, and P for (a) C_3-PMo_{12}, (b) C_4-PMo_{12}, (c) C_5-PMo_{12}, (d) C_6-PMo_{12}, and (e) C_{12}-PMo_{12}.

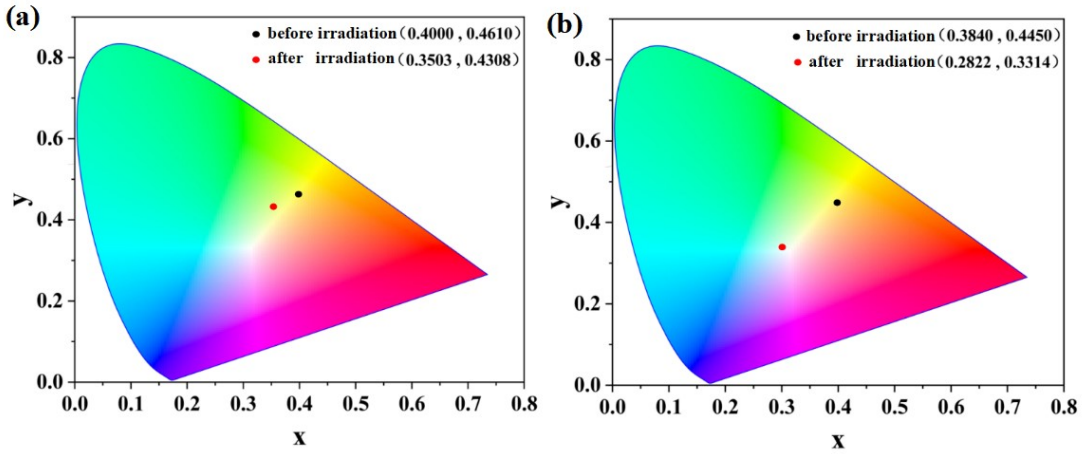


Fig. S9. (a, b) CIE chromaticity diagrams of C_3-PMo_{12}, C_6-PMo_{12}, before and after irradiation with a Xe lamp.

Table S1. L*, a*, b*, and ΔE values of C_3-PMo_{12}, C_6-PMo_{12}, and C_{12}-PMo_{12} before and after irradiation with a Xe lamp.

Sample	Before irrdation			After irrdation			ΔE
	L*	a*	b*	L*′	a*′	b*′	
C_3-PMo_{12}	82.891	-12.430	58.740	60.540	-16.440	29.120	29.960
C_6-PMo_{12}	83.450	-13.230	49.730	33.650	-7.590	-2.210	72.360
C_{12}-PMo_{12}	85.630	-13.238	6.912	24.910	-3.320	-6.940	85.040

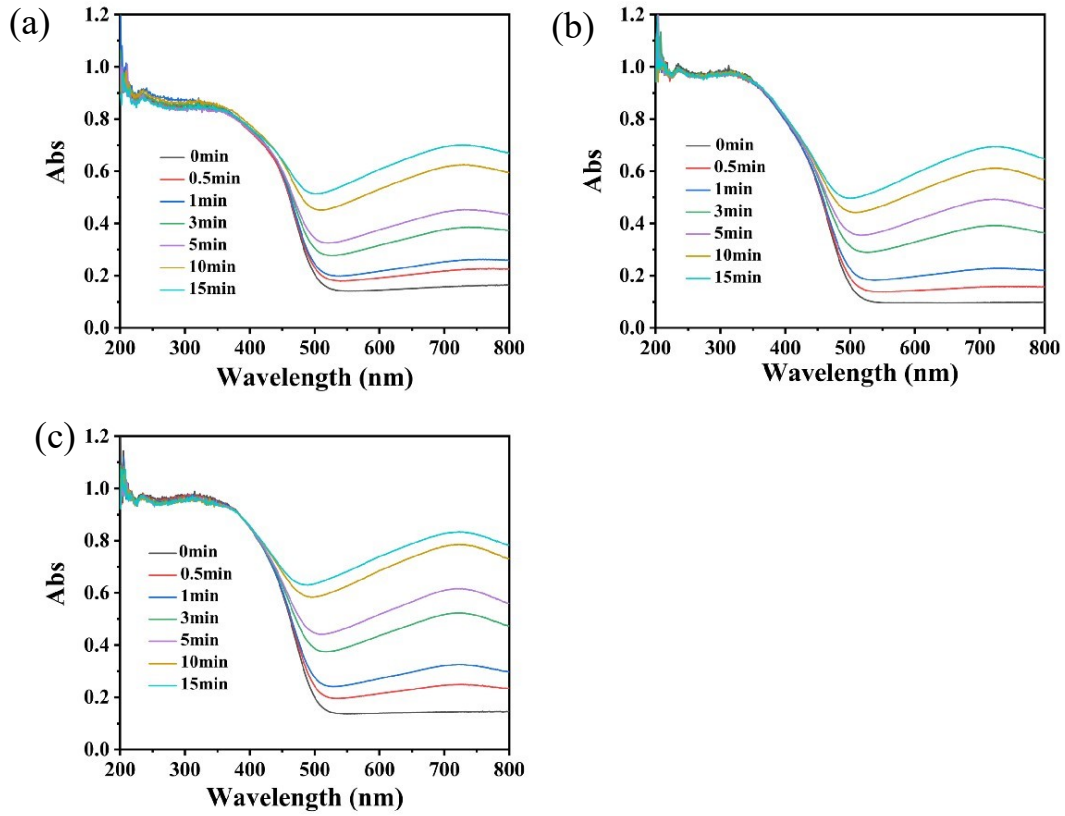


Fig. S10. (a-c) UV-vis spectra of compound C_3-PMo_{12}, C_4-PMo_{12}, and C_5-PMo_{12} before and after irradiation with a Xe lamp.

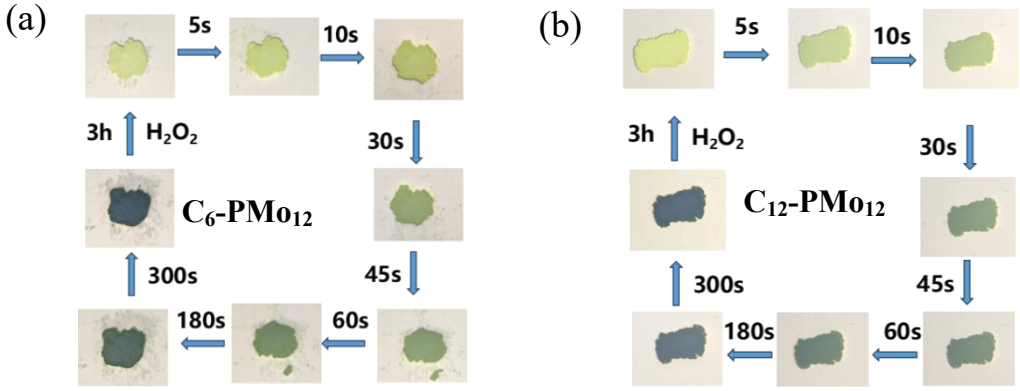
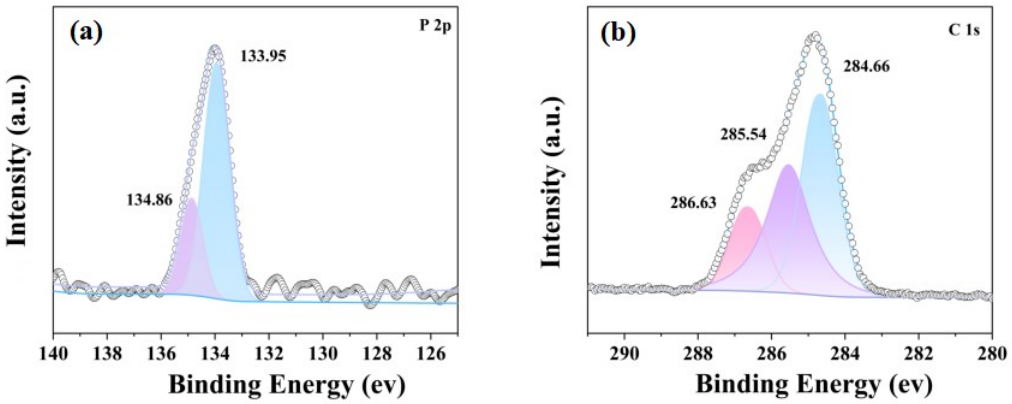


Fig. S11. (a, b) Compound C_6-PMo_{12}, C_{12}-PMo_{12} with a Xe lamp and in H_2O_2 atmosphere.

Before irradiation:



After irradiation:

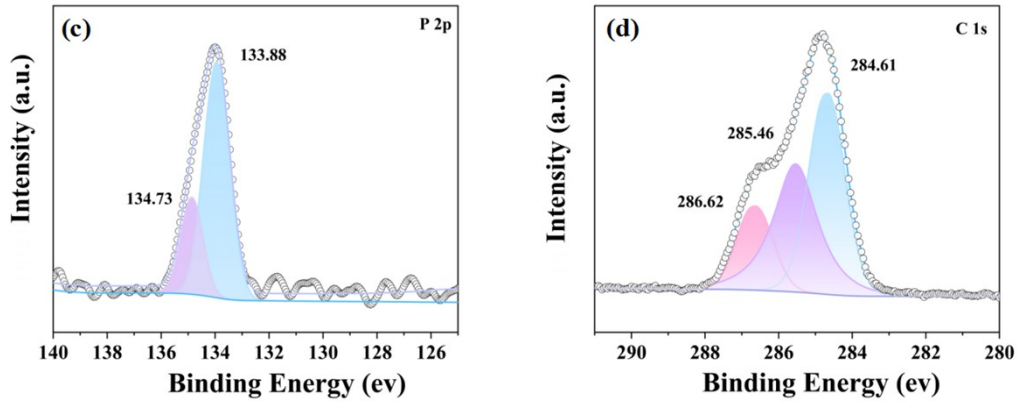


Fig. S12. (a-b) High resolution XPS spectra for C_{12}-PMo_{12} P2p (a), C1s (b) before irradiation. (c-d) High resolution XPS spectra for C_{12}-PMo_{12} P2p (c), N1s (d) after irradiation.

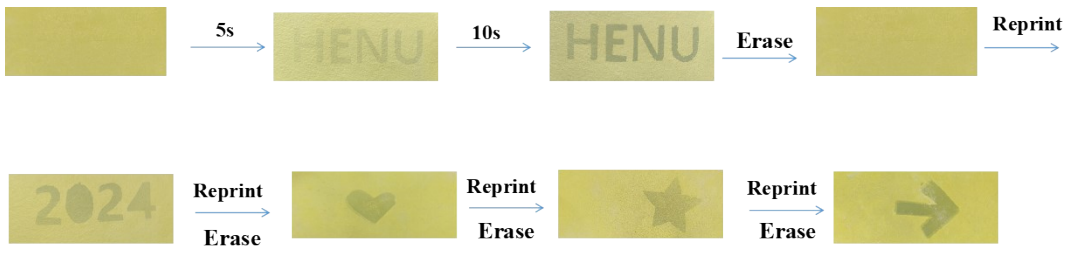


Fig. S13. Photographs of a pattern printed on C_6-PMo_{12} without ink under light irradiation.

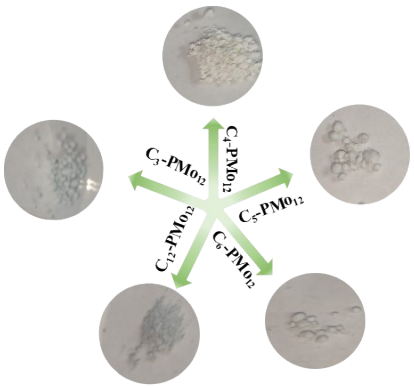


Fig. S14. Color change of C_n-PMo_{12} after detection for 3min of organic amine.

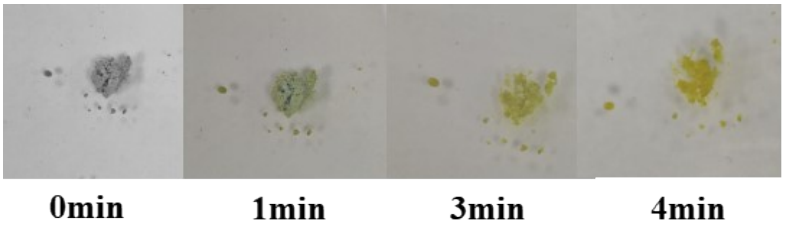


Fig. S15. Color change of C_{12}-PMo_{12} (after detection of organic amine) in HCl.

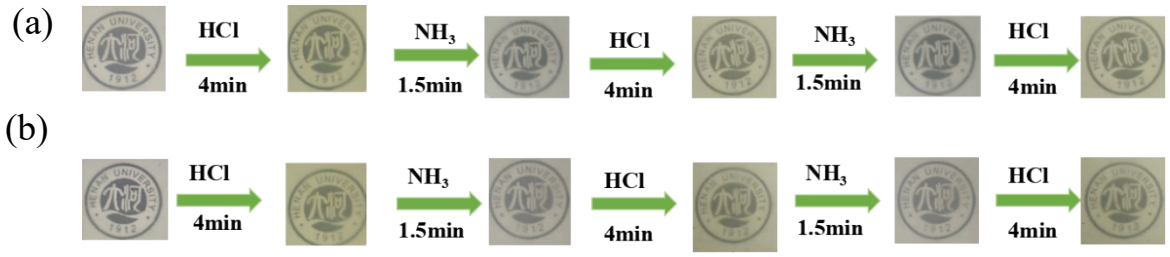


Fig. S16. (a-b) The Color change of (a)C_6-PMo_{12}-a, (b)C_{12}-PMo_{12}-b in HCl and organic amine.

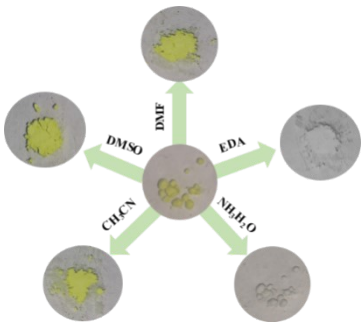


Fig. S17. Color change of C_{12}-PMo_{12} after detection of different solvent atmospheres of organic amine.