

One-pot Synthetic Strategy *via* Tandem Suzuki/Heck Reactions for the Construction of Luminescent Microporous Organic Polymers

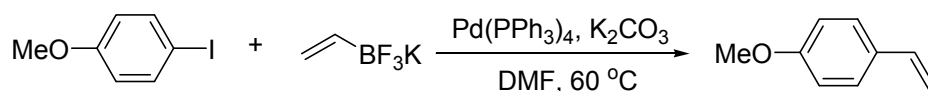
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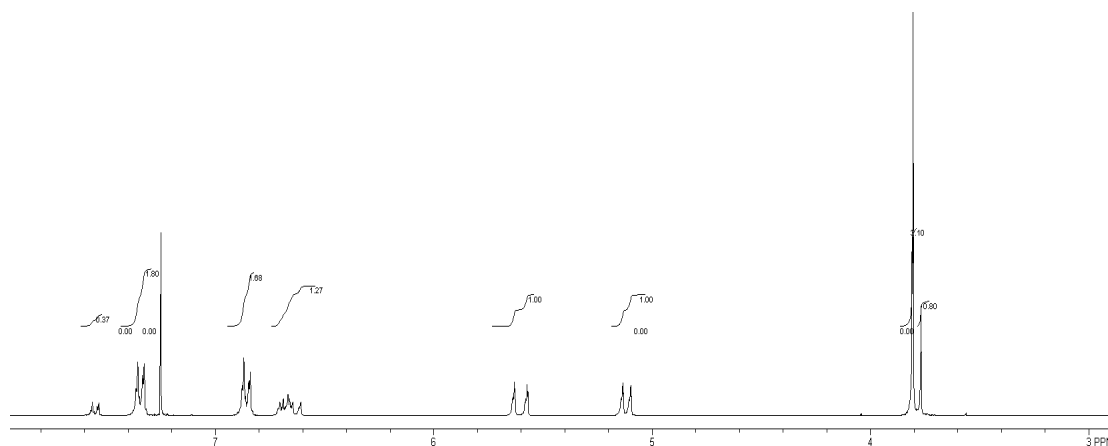
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EXPERIMENTAL SECTION



4-Iodoanisole (0.150 g, 0.64 mmol), PVTFB (0.103g, 0.77 mmol), potassium carbonate (0.177g, 1.28 mmol) and DMF (3 mL) were added to a reaction tube. After the system was evacuated and filled up with nitrogen for 3 times, the catalyst $\text{Pd}(\text{PPh}_3)_4$ (0.025 g, 0.02 mmol) was added and the same evacuation process was done. Then the system was kept at $60\text{ }^\circ\text{C}$ and stirred for about 12 h. The reaction was quenched with water, extracted with ethyl acetate, washed with brine, and dried over MgSO_4 . The product was obtained through flash column chromatography (petroleum ether as the eluate). Only 4-methoxystyrene was formed and 1,2-bis(4-methoxyphenyl)ethene was not observed. The ^1H NMR spectrum shows the ratio of 4-methoxystyrene/4-iodoanisole is ca. 3.9:1. These results indicate that only Suzuki reaction takes place at $60\text{ }^\circ\text{C}$ in this tandem reaction system.



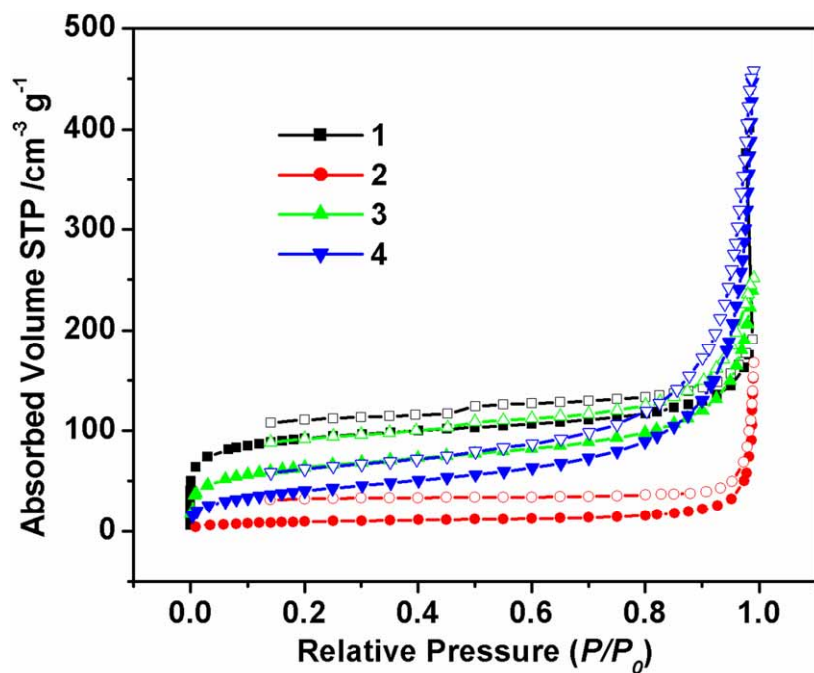


Fig. S1 N₂ adsorption-desorption isotherms measured at 77K for **LMOP-9**. The numbers 1-4 inset represent the polymers produced through several conditions, which are listed in **Table S1**.

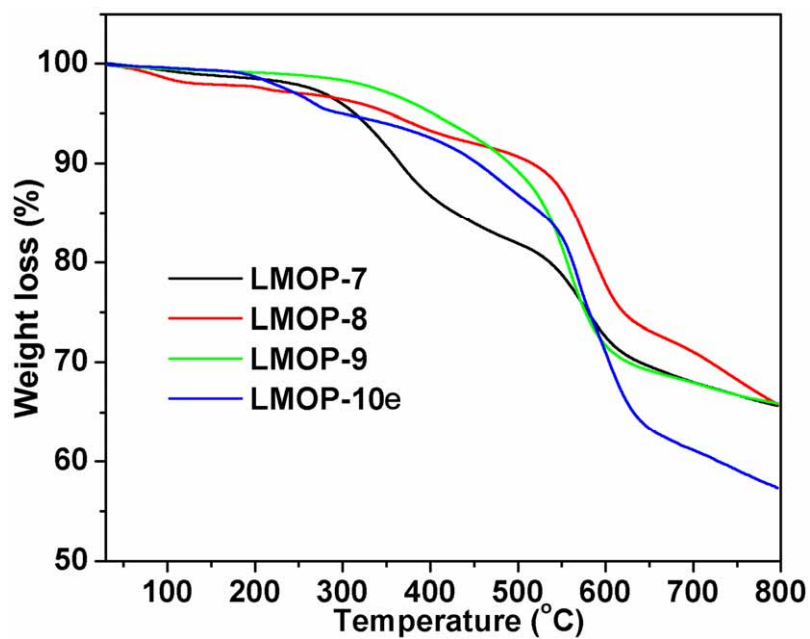


Fig. S2 The TG curves of LMOPs under N₂.

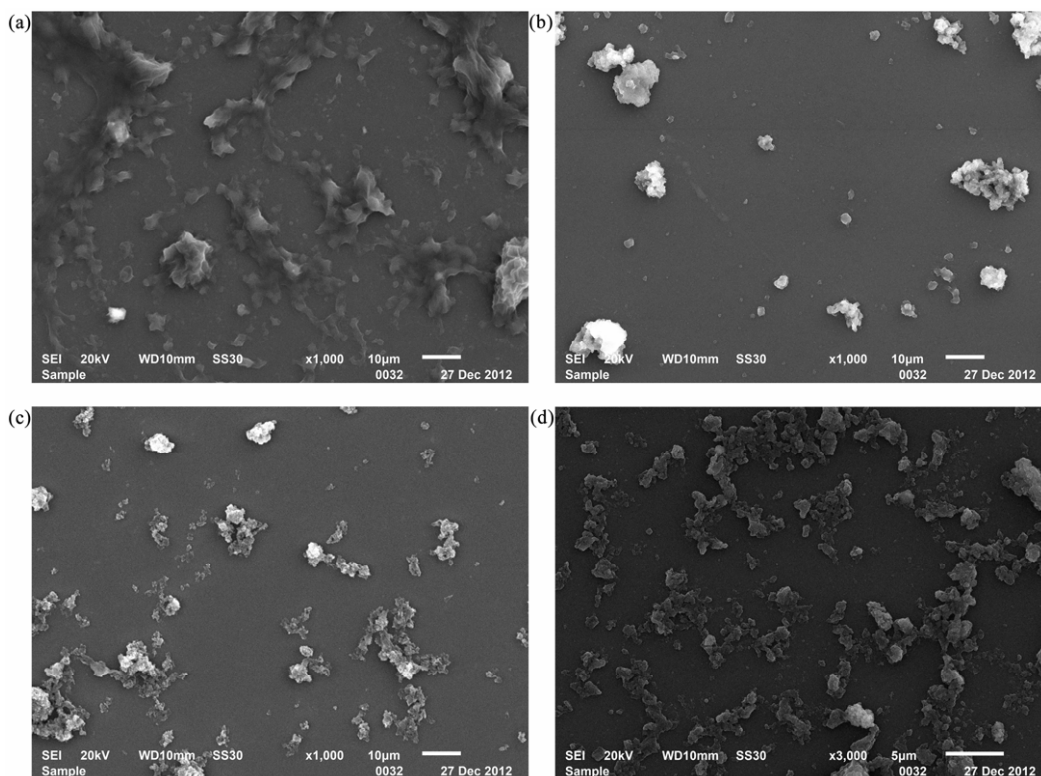


Fig. S3 Scanning electron microscope images for **LMOP-7** (a), **LMOP-8** (b), **LMOP-9** and **LMOP-10e** (d) at different magnifications. The samples were sputter-coated with gold before analysis.

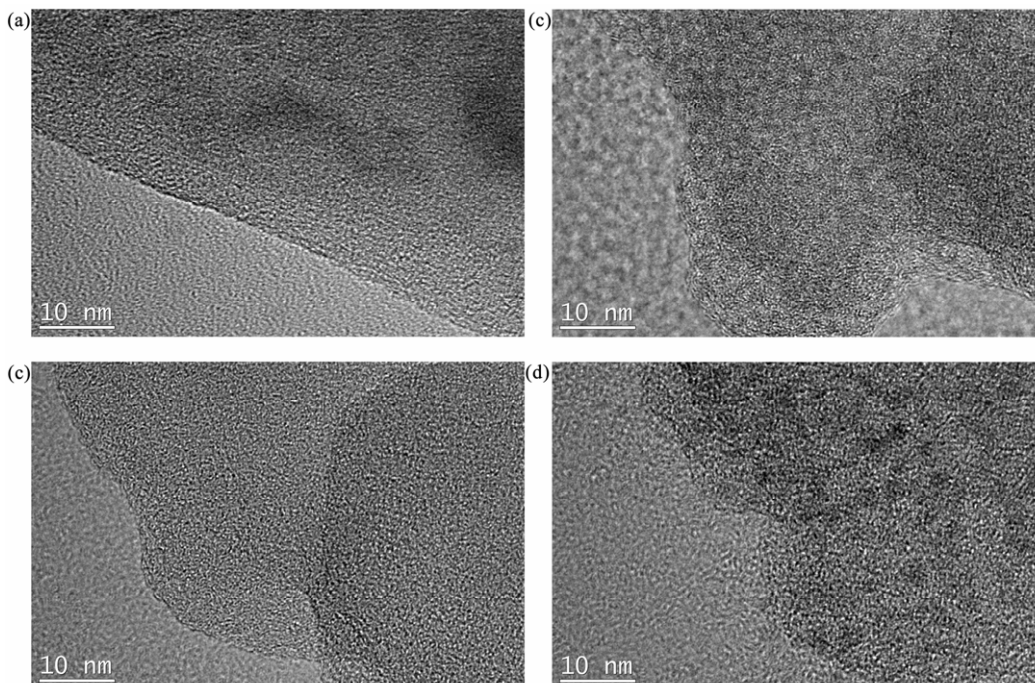


Fig. S4 Transmission electron microscopy images for **LMOP-7** (a), **LMOP-8** (b), **LMOP-9** (c) and **LMOP-10e** (d).

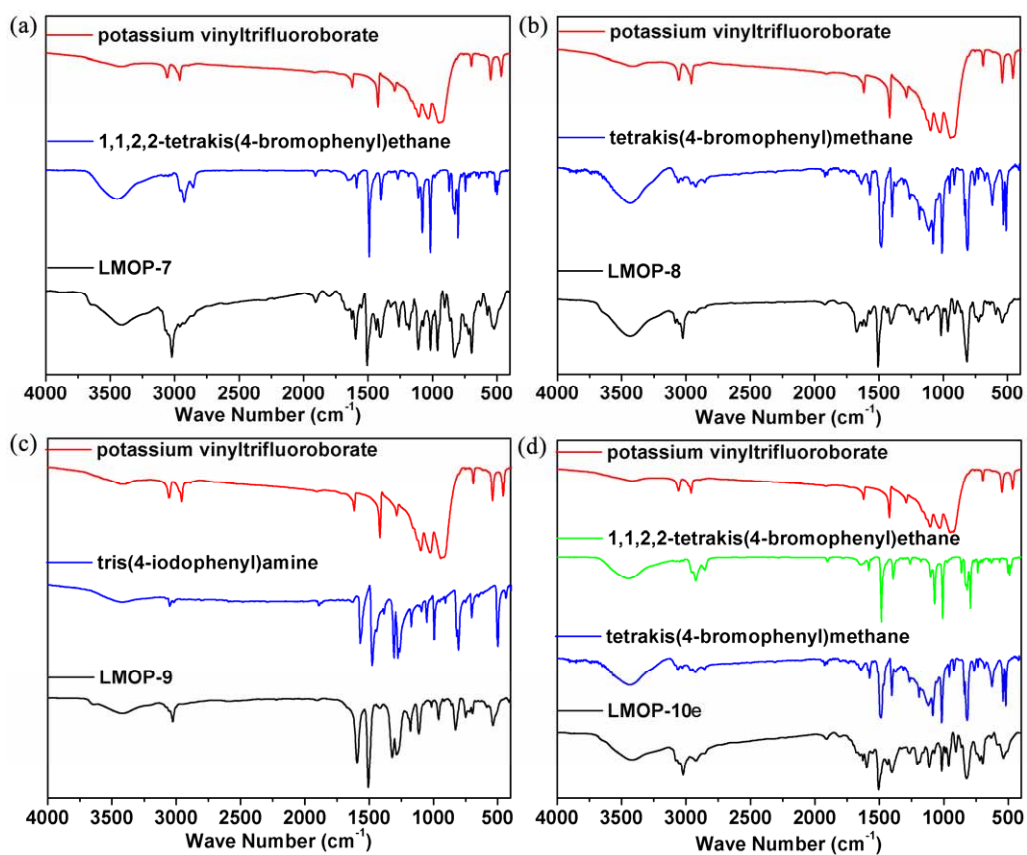


Fig. S5 FT-IR spectra of potassium vinyltrifluoroborate (PVTFB), aromatic halides and **LMOPs**: (a) PVTFB, TBPE and **LMOP-7**; (b) PVTFB, TBPM and **LMOP-8**; (c) PVTFB, TIPA and **LMOP-9**; (d) PVTFB, TBPE, TBPM and **LMOP-10e**.

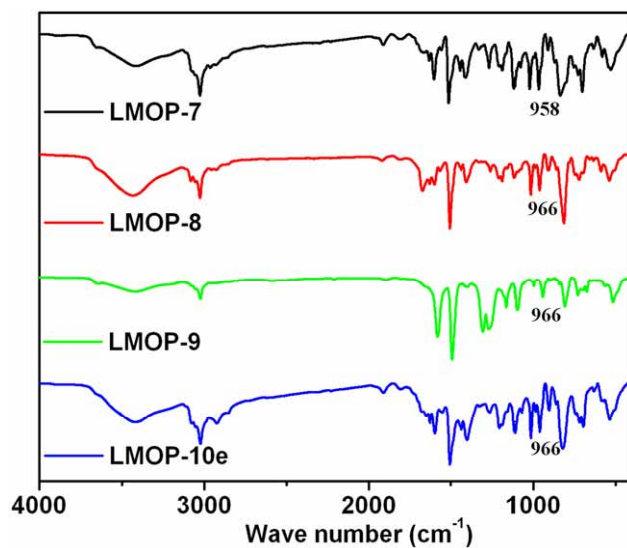


Fig. S6 FT-IR spectra of **LMOPs**.

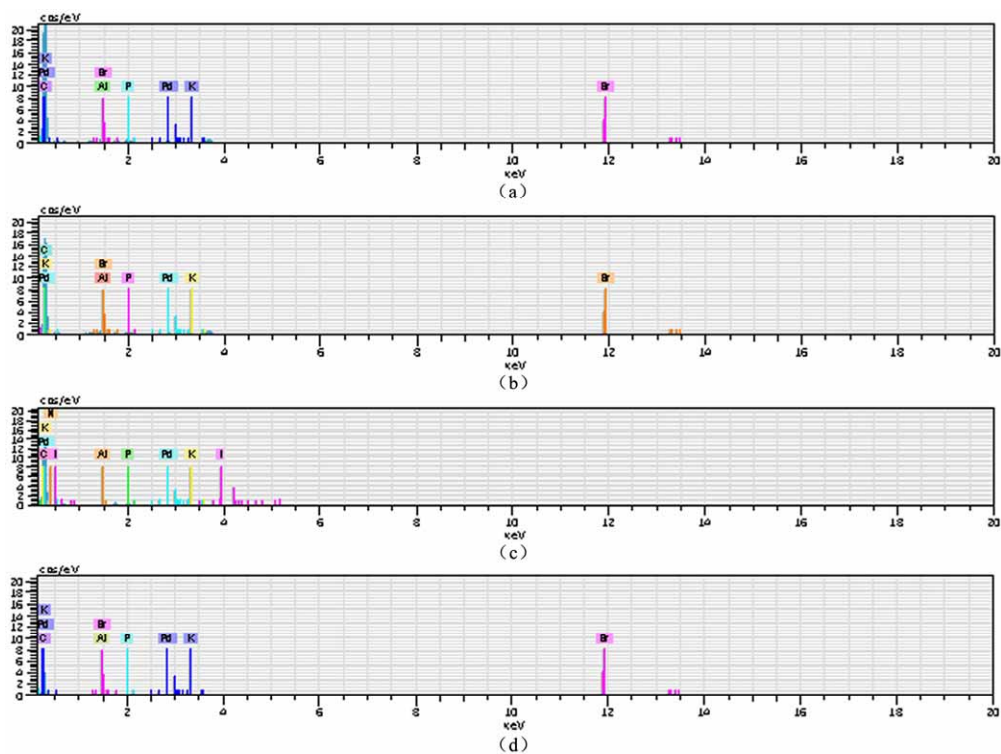


Fig. S7 EDX spectra of LMOPs.

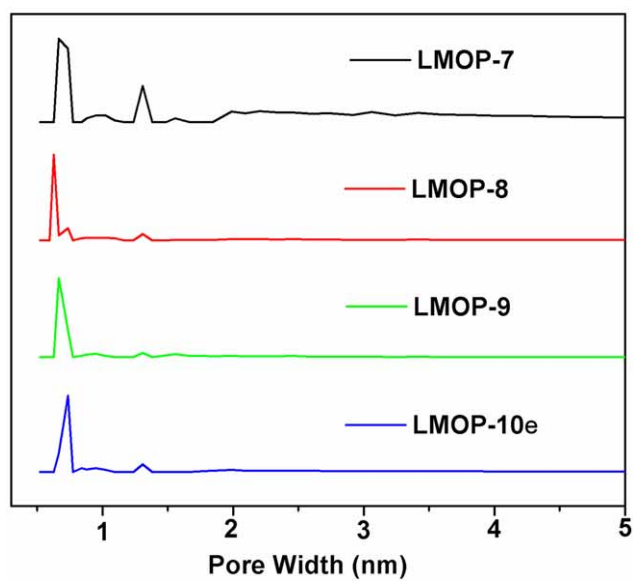


Fig. S8 The pore size distribution of LMOPs calculated by the NLDFIT method.

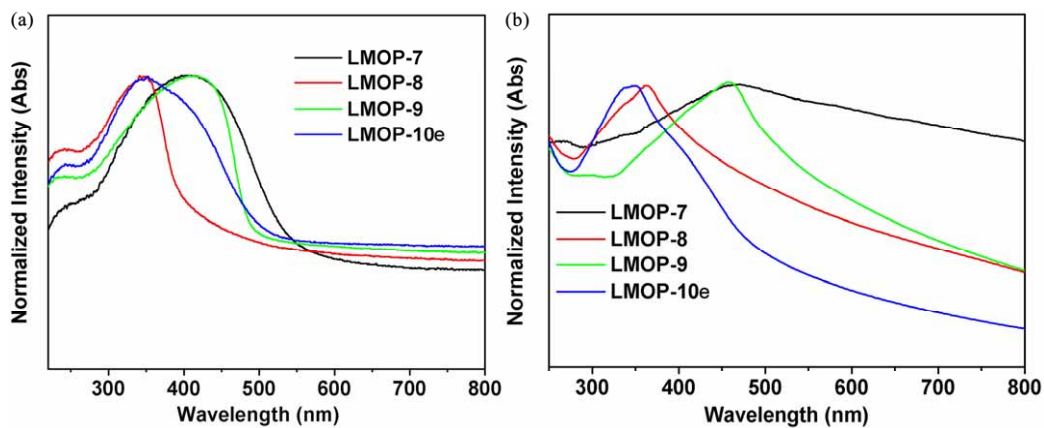


Fig. S9 UV-vis absorption spectra for LMOPs in solid state (a), ethanol (b).

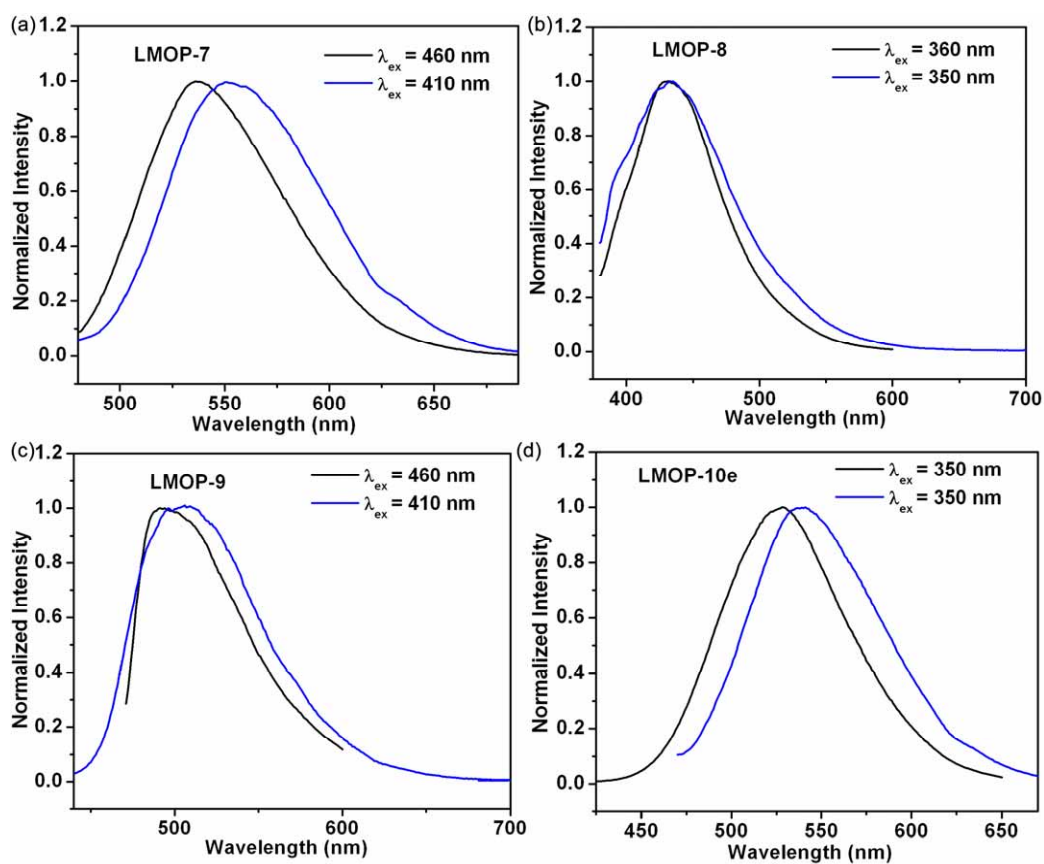


Fig. S10 Luminescent spectra for LMOPs in the solid state (blue) and ethanol (0.05 mg/mL, black).

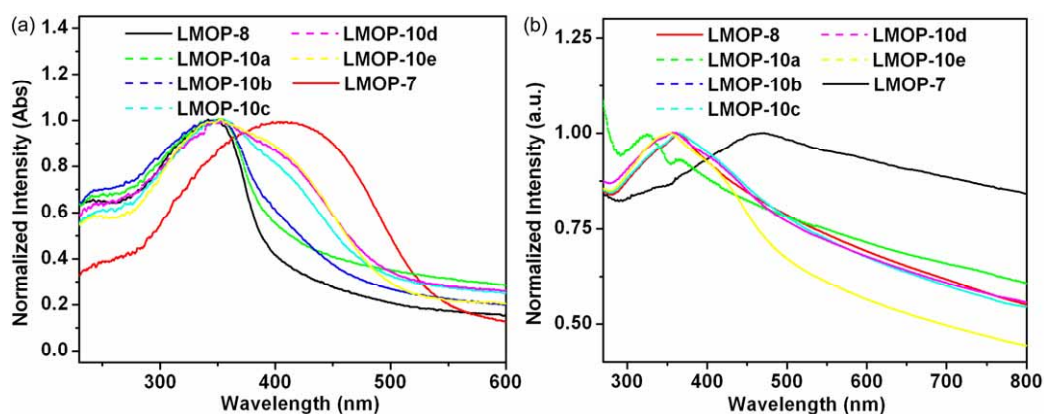


Fig. S11 UV-vis absorption spectra for **LMOP-10a-e** (TBPE:TBPM = 1:99, 5:95, 15:85, 30:70, 50:50) in solid state (a) and ethanol (b).

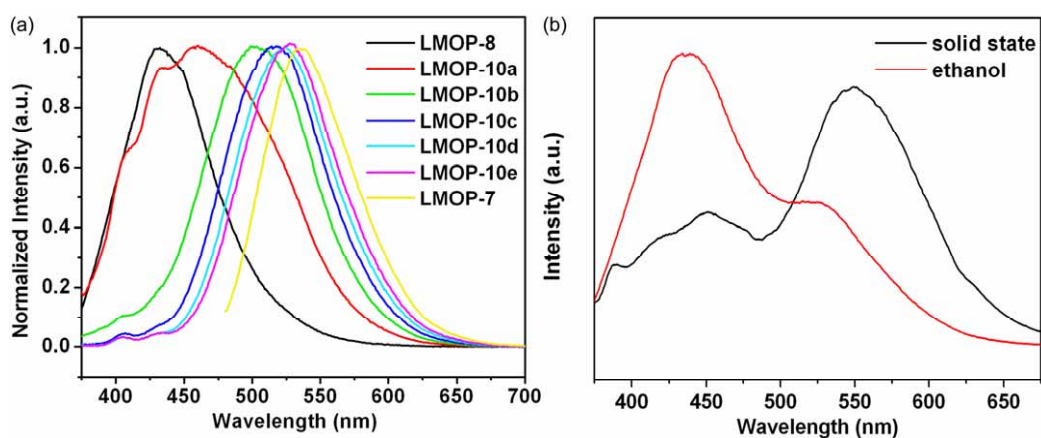


Fig. S12 (a) Luminescent spectra of **LMOP-10a-e** (TBPE:TBPM = 1:99, 5:95, 15:85, 30:70, 50:50) in ethanol. (b) The emission spectra for mechanically ground mixture of **LMOP-7** and **LMOP-8** (1:1) in the solid state ($\lambda_{\text{ex}} = 350$ nm) and ethanol ($\lambda_{\text{ex}} = 360$ nm).

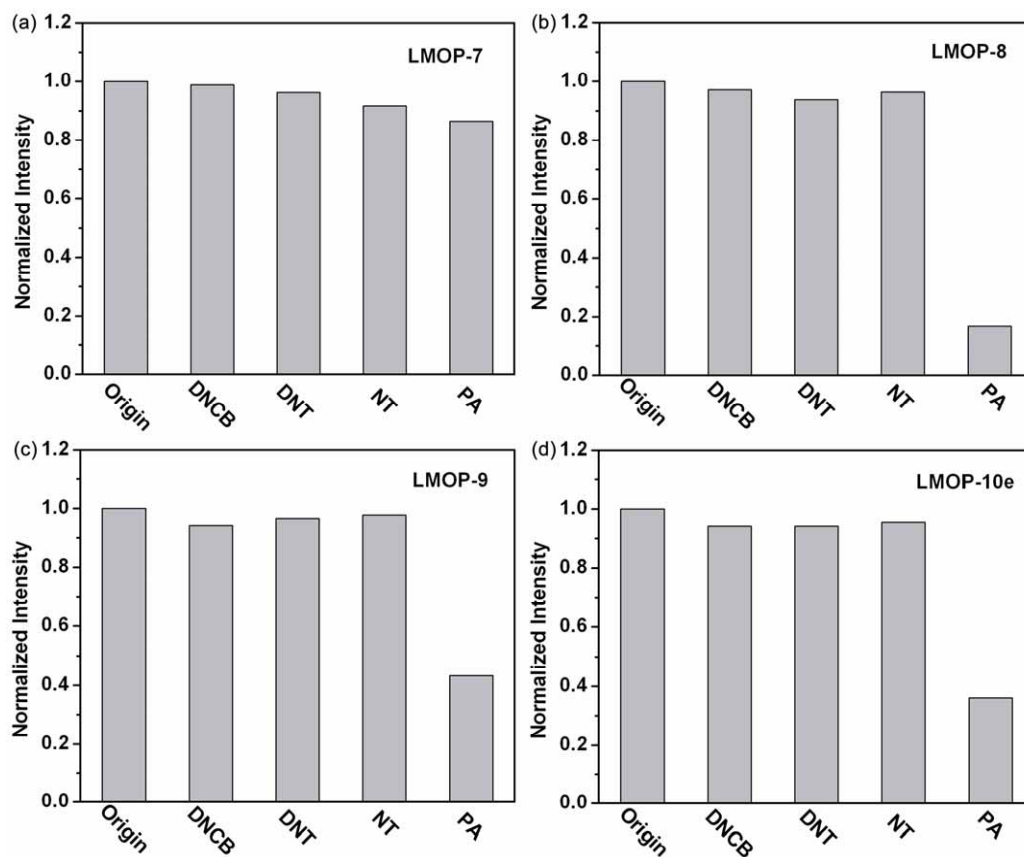


Fig. S13 The normalized luminescent intensity of LMOPs (a: LMOP-7, b: LMOP-8, c: LMOP-9, d: LMOP-10e) in ethanol upon addition of ca. 46.5 μM different analytes (DNCB: 2,4-dinitrochlorobenzene; DNT: 2,4-dinitrotoluene; NT: 4-nitrotoluene; PA: picric acid).

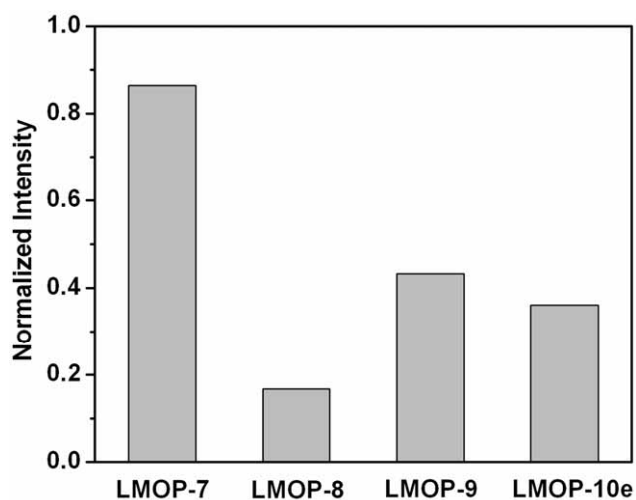


Fig. S14 The normalized luminescent intensity of LMOPs in ethanol upon addition of ca. 46.5 μM PA.

Table S1 BET surface areas of **LMOP-9** under different synthetic conditions.

Entry	Conditions	$S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$
1	Pd(PPh ₃) ₄ +K ₂ CO ₃ +DMF	318.32
2	Pd(PPh ₃) ₄ +K ₂ CO ₃ +DMSO	33.99
3	Pd(PPh ₃) ₄ + Diisopropylamine +DMSO	225.77
4	Pd(PPh ₃) ₄ +Cs ₂ CO ₃ +DMSO	148.60

Table S2 EDX analyses of **LMOPs**.

LMOPs	wt. %				at. %			
	C	Br	I	Pd	C	Br	I	Pd
LMOP-7	94.58	2.75	-	1.35	98.85	0.43	-	0.16
LMOP-8	92.36	5.78	-	1.05	98.62	0.93	-	0.13
LMOP-9	90.56	-	1.05	1.17	94.12	-	0.10	0.14
LMOP-10e	93.45	0.10	-	1.55	97.60	0.02	-	0.18

Table S3 Texture properties of **LMOPs**.

LMOPs	$S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$	$S_{\text{Langmuir}}/\text{m}^2 \text{g}^{-1}$	$S_{\text{micro}}/\text{m}^2 \text{g}^{-1}$	$V_{\text{total}}^a/\text{m}^3 \text{g}^{-1}$	$V_{\text{micro}}^b/\text{m}^3 \text{g}^{-1}$
LMOP-7	488	633	153	0.444	0.067
LMOP-8	639	932	336	0.601	0.153
LMOP-9	318	429	169	0.251	0.077
LMOP-10e	487	658	198	0.375	0.089

^a Total volume at P/Po = 0.97. ^b The micropore volume calculated from *t*-plot method.