

**Luminescent and Swellable Conjugated Microporous
Polymers for Detecting Nitroaromatic Explosives and
Removing Harmful Organic Vapors[†]**

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Abstract

Four new conjugated microporous polymers (CMPs) were synthesised by Buchwald-Hartwig cross-coupling reaction of tri- and tetra- functionalised precursors to yield materials with tuneable surface area and pore size distribution. This approach yielded **LPCMP1 – 4**, CMPs with significantly higher Brunauer–Emmett–Teller (BET) surface area (more than five times higher) than other related BH-based CMPs. These CMP materials possess not only high BET specific surface areas and high chemical and thermal stabilities, but also exhibit outstanding swellability. To the best of our knowledge, swellable behaviour was found for CMPs for the first time, with the greatest degree of swelling for methanol reaching 16.5 and 16.3 mL g⁻¹ for of **LPCMP1** and **LPCMP3**, respectively. Owing to their excellent swellability, we further studied the adsorption capacity of these CMPs for different toxic organic vapours (including toluene and methanol). **LPCMP1** and **LPCMP3** adsorbed 124 mg g⁻¹ and 117 mg g⁻¹ respectively, toluene at its saturated vapor pressure. For methanol, the adsorption capacities of **LPCMP1** and **LPCMP3** were up to 250 mg g⁻¹ and 215 mg g⁻¹, respectively, which is the highest recorded value when compared with published data for CMPs, HCPs, MOFs and porous carbons. These materials are promising candidates for the removal and elimination of hazardous organic vapors and chemical warfare agents. Moreover, all the polymers exhibit strong luminescence and show high sensitivity to nitroaromatic explosives. **LPCMP2** **LPCMP4**, exhibit high selectivity for TNT, and may be suitable as new candidates to selectively detect TNT for security or environmental applications.

Introduction

Porous organic polymers (POPs) are a class of highly crosslinked porous polymers mainly composed of light elements such as C, N, O, H and B. These polymers show outstanding chemical and physical stability, high surface area, well-defined porosity and low skeletal density.¹ Owing to their exceptional properties, a large number of POPs have already been prepared, including conjugated microporous polymers (CMPs),^{2,3} covalent organic frameworks (COFs),^{4,5} polymers of intrinsic micro-porosity (PIMs),^{6,7} porous aromatic frameworks (PAFs)⁸ and hyper-crosslinked polymers (HCPs).⁹

Among these, CMPs permit the linking of building blocks in a π -conjugated fashion and possess three-dimensional (3D) networks. A range of different types of C–C coupling reactions, including Suzuki,¹⁰ Sonogashira–Hagihara,¹¹ Yamamoto,¹² ethynyl trimerization reaction¹³ and carbazole–based oxidative coupling polymerization¹⁴ have been applied to synthesize CMPs. Compared with MOFs, the strong covalent bonds formed by these coupling reactions afford attractive properties, including higher thermal and chemical stabilities. Compared to non π -conjugated HCPs and COFs, the extended π -conjugated nature of the networks endows them with unique electron-donating characteristics and good luminescence properties.¹⁵ Unlike porous carbon materials, the vast choice of organic building blocks with different functional groups that have been used to synthesize CMPs not only allow fine-tuning of the specific surface area and porosity of the polymers,¹⁶ but also provide impressive diversity of properties and functionalities.¹⁷ Owing to these outstanding features, CMPs have shown great potential for application in gas adsorption and separation,¹⁸ chemosensors,^{19,20} photocatalysis¹⁷ and energy storage.²¹

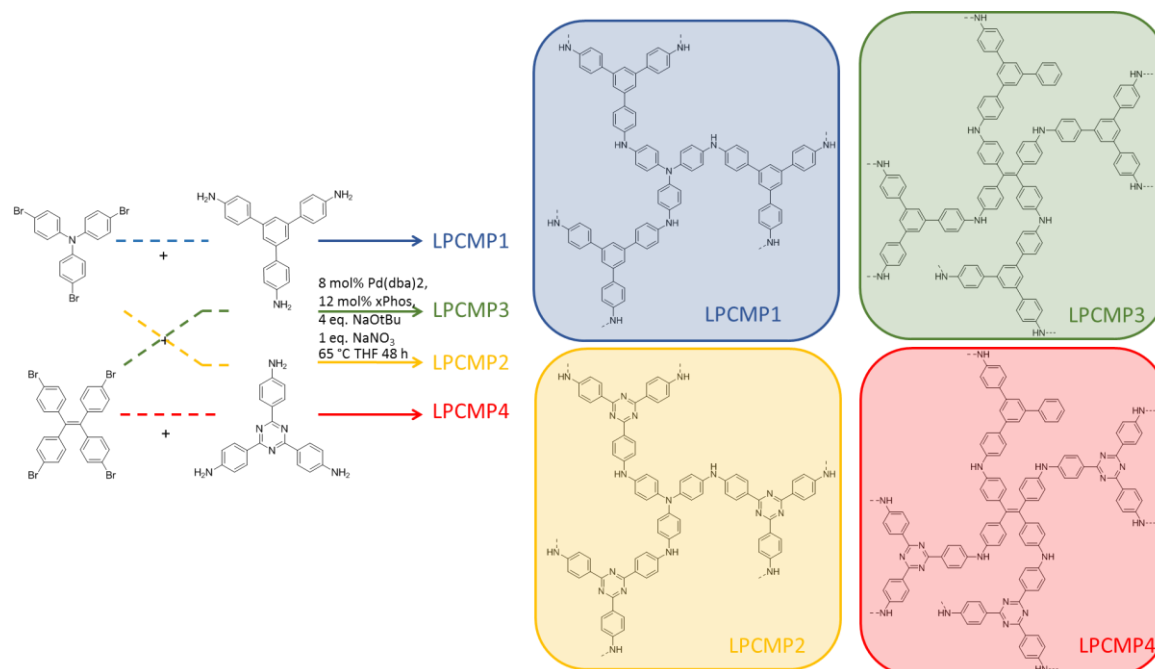
Swellability, one of the lesser-known physical properties of crosslinked porous polymers, has not been studied thoroughly, nor attracted significant attention. In contrast to MOFs and porous

carbon materials, the high number of links introduced by the crosslinking reaction provides the opportunity to create weak inter-chain interactions during removal of the reaction solvent to form the dry polymer network.²² The internal stress created during the drying process can be relieved by the polymeric network allowing for the expansion of the formed structure, thus creating a swellable porous network. The swellability can be affected by several parameters, including the initial monomer concentration,²³ the extent of crosslinking and the solvation state of the growing polymer chains (nature of reaction solvent) during the polymerisation.²⁴ The polarity of the polymer will also influence its swellability.²⁵ The swellability of HCPs has led to their use in various applications such as trapping of organic vapors,²⁶ ion exchange,²⁷ removal of toxic trace metals,²⁸ solid phase extraction,²⁹ and recovery of organic pollutants from water.³⁰

Keeping applications in mind, detection of nitroaromatic explosives has become a critical issue and attracted substantial interest for public security, environmental safety and military applications.³¹ Detecting explosives in solution, in addition to detection in the vapour phase, is also critical.³² Trinitrotoluene (TNT), as one of the most commonly and widely used explosives for military, industrial, and mining applications, is considered a serious environmental contaminant with potential harmful and toxic effects on animals, plants, and humans.^{33,34} Thus, it is crucial to detect TNT and its derivatives as early as possible in soil, groundwater, or waste streams. Fluorescent conjugated polymers have attracted attention for use in chemical sensors owing to their high specific surface area, permanent porosity, good chemical and physical stability.³⁵ However, there are limited reports about luminescent CMPs used for the detection of nitroaromatic compounds,^{19,20} and therefore provides further opportunities for the introduction of new materials for this important application area.

Inspired by these developments and potential applications, and keen to continue to exploit the Buchwald–Hartwig (BH) cross-coupling strategy for CMP production, we here extend the amine-CMP family by using 1,3,5-tris(4-bromophenyl)amine (TBPA), tetrakis(4-bromophenyl)ethylene (TBPE), 1,3,5-tris(4-aminophenyl)benzene (TAPB) and 1,3,5-tris-(4-aminophenyl)triazine (TAPT) as building blocks (please see Figure S10 for other cores and linkers employed in our earlier investigations). The approach to date has been to select and combine cores with multiple Br groups and various di-amine linkers. In this study, we expand our synthetic approach and use combinations of tri- and tetrabromo and -amine building blocks (see Scheme 1) to synthesize four novel BH CMPs and explore their properties and applications.

Result and Discussion.

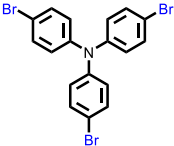

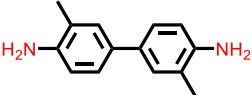
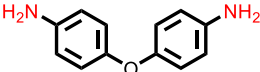
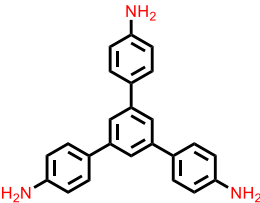


Scheme 1. Synthetic route for the production of **LPCMP1-4**

The synthesis route for the four CMPs is depicted in **Scheme 1**. A series of optimization experiments were performed for the synthesis of **LPCMP1** in order to obtain the highest yield and specific surface area. As shown in Table S1, different solvents, variation of the concentrations and ratio of the two building blocks were investigated and the best yield observed was 62% with a surface area of 275 m² g⁻¹. A comparison of the **LPCMP1-NS** (no added inorganic salt – see below) with other CMPs obtained by BH cross coupling of a brominated core and diamine linker pattern is shown in **Table 1**. The **LPCMP1-NS**, which was synthesized using the triamine building block, exhibited a significantly higher BET surface area (more than five times higher) than the other BH-based CMPs which were synthesized using the same core. Full synthetic control of the surface area and porosity of BH-based CMPs by the addition of inorganic salts, the so-called Bristol-Xi'an Jiaotong (BXJ) method, was reported by our group recently.¹⁶ We found that the addition of simple salts tuned the Hansen

solubility parameters (HSPs) of the solvents to match that of the growing polymer chains, leading to CMPs with significantly higher surface areas and well-defined micropores. In order to further improve the surface area of **LPCMP1**, sodium nitrate (NaNO_3) was thus added to the reaction system. The yield increased from 62% to 98% and the BET specific surface area increased dramatically from $275 \text{ m}^2 \text{ g}^{-1}$ to $1280 \text{ m}^2 \text{ g}^{-1}$. Similar optimization experiments were also performed for the remaining CMPs and the final reaction conditions are shown in the SI page 5.

Table 1. A comparison of the **LPCMP1-NS** with the other CMPs which were synthesized using the same core.

Core	Linker	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	Ref
		52	37
		62	37
		44	unpublished
		275	This work

The thermal stability of the polymers was studied (Figure S1); all the polymers possess good thermal stability and $\sim 5\%$ mass loss was observed from 300 to $370 \text{ }^\circ\text{C}$ under a nitrogen atmosphere. Owing to their cross-linked nature, there is no distinct glass transition until $800 \text{ }^\circ\text{C}$. SEM images of the polymers are presented in Figure S2, showing micrometer-sized amorphous polymer particles. The solid-state UV–Vis absorption spectra and photoluminescence emission spectra of **LPCMP1–4** are shown in Figure S7. All the polymers possess good fluorescence and owing to the extended π conjugated structure in the CMPs, broad emission peaks at 500 nm , 558 nm , 536 nm and 611 nm , respectively, were observed.

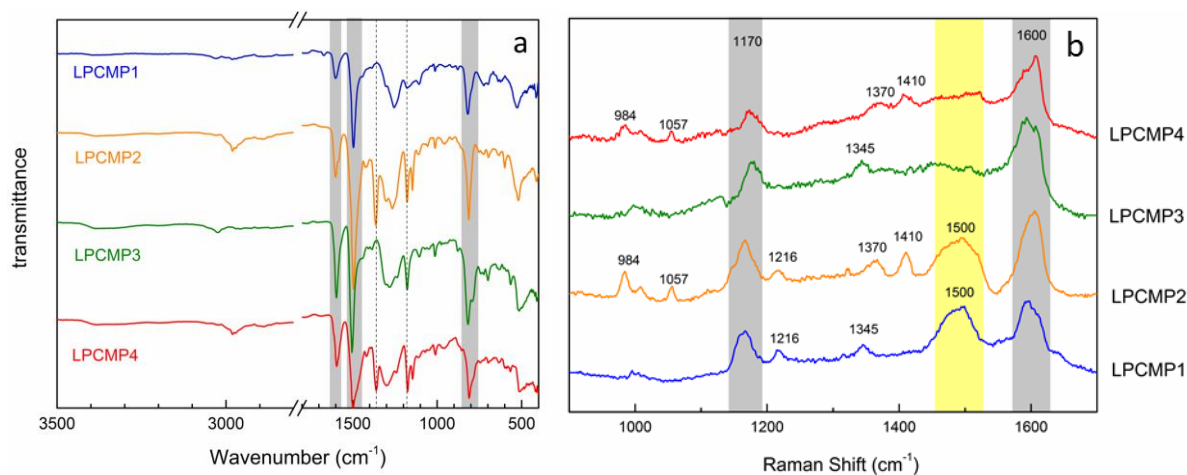


Figure 1. FT-IR (a) and Raman spectra (b) of **LPCMP1–4**

Comparison of the FT-IR spectra of the four polymers (**Figure 1**) show similarities, such as the peaks at 1600 cm^{-1} , 1500 cm^{-1} , 1280 cm^{-1} and 810 cm^{-1} , which are attributed to the stretching vibrational bands of benzenoid-type secondary amine ($-\text{Ph}-\text{NH}-$), stretching vibrations of the aromatic ring skeleton, stretching vibrational bands of C–N and bending vibrations of $-\text{CH}-$ from substituted benzene, respectively. In contrast to **LPCMP1** and **LPCMP3**, a peak at approximately 1360 cm^{-1} was observed for **LPCMP2** and **LPCMP4**, which is the characteristic stretching vibrations of the triazine ring. The Raman spectra of all the polymers are shown in **Figure 1**. All the **LPCMPs** showed two similar peaks at around 1600 cm^{-1} and 1170 cm^{-1} , which are attributed to the C–C stretching of benzene rings and $-\text{CH}-$ in-plane bending from benzenoid rings. For **LPCMP2** and **LPCMP4**, the two weak absorption peaks at 984 cm^{-1} and 1057 cm^{-1} are the characteristic breathing vibrations of the triazine ring. The two weak peaks at 1370 cm^{-1} and 1410 cm^{-1} are assigned to the C–N stretching vibrations of aromatic amines. For **LPCMP1** and **LPCMP2**, a broad peak was observed at 1500 cm^{-1} , assigned to the C–N stretching vibration of the tertiary amine from the tris(4-bromophenyl)amine building block. All these peaks are consistent with the proposed structures of the polymers.

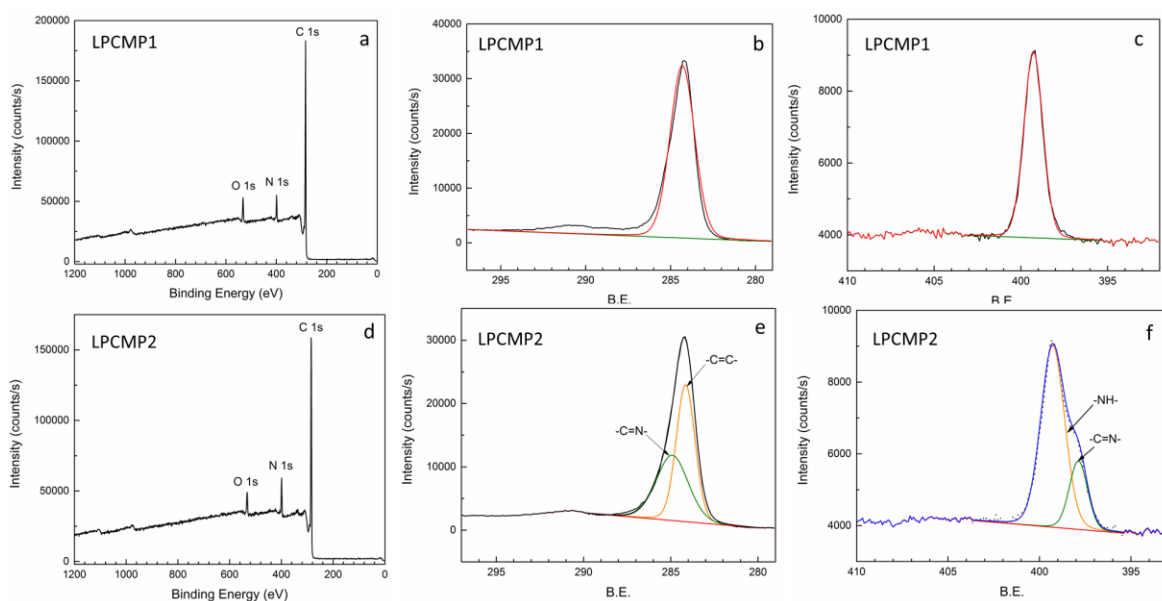


Figure 2. The X-ray photoelectron spectra of **LPCMP1** and **LPCMP2**. (b) and (e) are the high-resolution spectra of C 1s, and (c) and (f) are the high-resolution spectra of N 1s in the two samples, respectively.

In order to further confirm the structures of all the polymers, X-ray photoelectron spectroscopy (XPS) was used to validate the elemental composition and the chemical bond type. As shown in **Figure 2** and Figure S3, characteristic carbon and nitrogen peaks were observed in all spectra. The XPS results prove that there was no reaction between the CMP networks and the added inorganic salts, and that all salts were completely removed from the polymers (absence of sodium peaks). The high-resolution XPS spectra of C 1s and N 1s are shown in **Figure 2** and Figure S3. For **LPCMP1** and **LPCMP3**, a single peak of the aromatic C centred at 284 eV and a single peak of the amine N centred at 399 eV were observed. For **LPCMP2** and **LPCMP4**, which were constructed from the triazine building block (TPAP), the C 1s and N 1s spectrum could be deconvoluted into two peaks. The weaker peak at 285 eV for the C 1s and at 397 eV for N 1s are the characteristic C and N peaks of the $-C=N-$ moiety from the triazine building block. Solid-state ^{13}C and ^{15}N CPMAS spectra of **LPCMP3** and **LPCMP4** were also acquired (Figures S4 and S5), which were in good agreement with the proposed structures of **LPCMP3**

and **LPCMP4**. In particular, in the ^{13}C CPMAS NMR spectrum of **LPCMP4**, an additional signal is observed at 171 ppm compared to the ^{13}C CPMAS NMR spectrum of **LPCMP3** (Figure S4), which is attributed to the carbon atoms of the triazine fragment (see the corresponding structures in Scheme 1). The sensitivity of the natural abundance ^{15}N CPMAS NMR measurements was sufficient to detect the protonated NH groups only, with the chemical shifts of -297 ppm in **LPCMP3** and -288 ppm in **LPCMP4** (Figure S5).

To study the porosity of the materials, sorption analysis using nitrogen as the sorbate molecule was performed. Nitrogen adsorption–desorption isotherms for all the CMPs measured at 77 K are shown in **Figure 3**. A combination of type I and II nitrogen sorption isotherms, according to the IUPAC classification,³⁸ were observed for all the polymers. All polymers possess microporous features, which can be inferred from the rapid uptake at a low relative pressure ($P/P_0 = 0-0.1$) shown in the nitrogen adsorption–desorption isotherms. However, the uptake did not reach a plateau, which suggests that swelling of the polymer matrices occurred. Upon desorption, a large hysteresis and an open isotherm were observed, caused by the restricted diffusion of the N_2 adsorbate.³⁹ The large hysteresis is also indicative of swelling/trapping effects in the flexible polymeric networks, especially for amorphous microporous organic polymers.^{40,41} The BET specific surface area values of **LPCMP1–4** are listed in **Table 2**. **LPCMP1** and **LPCMP3**, synthesized by using 1,3,5-tris(4-aminophenyl)benzene as building block, possess similar BET specific surface area values, much higher than **LPCMP2** and **LPCMP4** that were synthesized with 1,3,5-tris(4-aminophenyl) triazine as building block. One possible reason for the difference in the BET surface area is that the amino groups in the benzene building blocks are more active than the amino groups in the triazine building blocks when they undergo BH cross coupling and thereby produce polymers with a higher crosslinking degree.⁴² The pore size distribution (PSD) profile of the obtained materials is shown in **Figure 3**. **LPCMP2** and **LPCMP4** have similar pore size distributions, both with a dominant pore size

(0.72 nm). Compared with **LPCMP2** and **LPCMP4**, a larger dominant pore size located at 1.8 nm were found for **LPCMP1** and **LPCMP3**, which resulted in larger average pore sizes (1.5 and 1.9 nm, respectively). This finding demonstrates that the choice of building block is crucial for the specific surface area and pore size of the CMPs and, more importantly, that the surface area and pore size is tuneable by changing the building blocks.

The CO₂ uptake capacity of all the obtained N-containing **CMPs** was also studied. The CO₂ adsorption isotherms measured at 273 K are shown in Figure S6. **LPCMP1** and **LPCMP3**, possessing higher surface areas, exhibit the higher carbon dioxide storage of 3.4 and 3.3 mmol/g at 1.0 bar and 273 K, respectively (see Table 2). For **LPCMP2** and **LPCMP4**, owing to the higher nitrogen content of the triazine building block, the CO₂ uptake capacity still reached 2.5 and 2.2 mmol/g, respectively, despite the surface area being less than half of **LPCMP1** and **LPCMP3**.

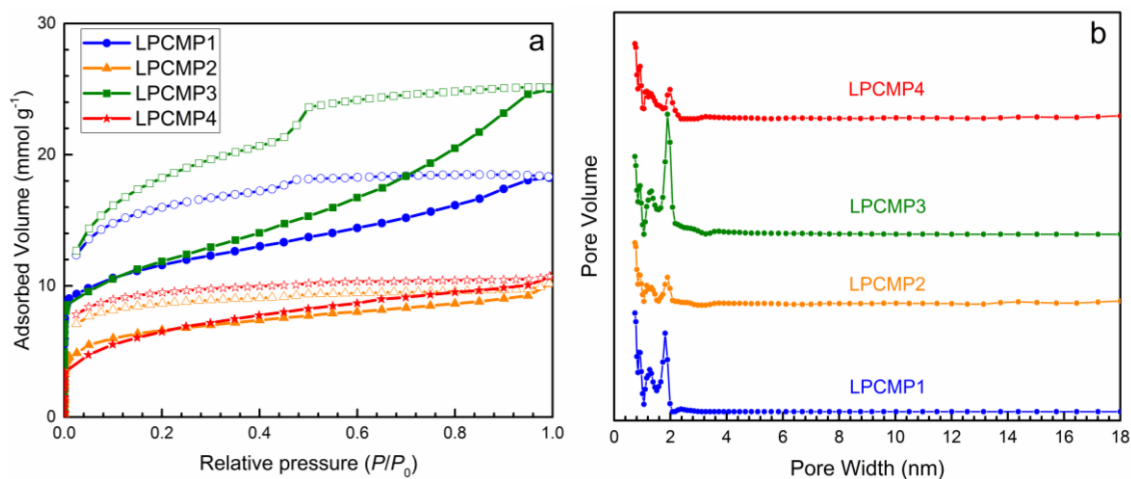


Figure 3. (a) N₂ adsorption–desorption isotherms of **LPCMP1–4** measured at 77 K; the adsorption and desorption branches are marked with solid and open symbols, respectively. (b) The PSD profiles of **LPCMP1–4** calculated by NLDFT.

Table 2. Porosity Properties and CO₂ Uptake Capacities of Polymers

Sample	S _{BET} (m ² g ⁻¹)	V _{total} (cm ³ g ⁻¹)	D _{pore} (nm)	CO ₂ uptake (mmol/g)
LPCMP1	1280	0.59	1.51	3.4
LPCMP2	516	0.30	0.74	2.5
LPCMP3	1340	0.79	1.90	3.3
LPCMP4	570	0.33	0.74	2.2

LPCMP1 and **LPCMP3** showed surprisingly good swellability after the polymers were washed and dried. Figure S8a shows **LPCMP1** after the washing and filtration procedure without further drying. Figure S8b shows **LPCMP1** after drying at 40 °C under vacuum. A significant change in the volume of **LPCMP1** was observed before and after drying: **LPCMP1** shrank 80% after drying. Similar volume changes have only been found in HCPs,³⁶ with such behaviour not reported before for CMPs – an exciting new development for this class of materials.

We carried out a series of experiments to quantify the swellability, Q , of the synthesised CMPs.³⁶ The Q values of **LPCMP1-4** in different solvents are listed in **Table 3**. The greatest degree of swelling was obtained for the **LPCMP1** and **LPCMP3** with methanol ($Q = 16.5$ and 16.3 mL g^{-1} respectively) and the least swelling obtained when DMF was used as the solvent ($Q = 8.1$ and 9.1 mL g^{-1} respectively). Notably, the Q values observed are even higher than the swelling of HCPs derived from in fluorobenzene and toluene (with Q values of 15.7 mL g^{-1} in DMF).³⁶ These results demonstrate that the novel CMPs possess unparalleled and uniquely flexible networks, fully consistent with the nitrogen sorption isotherms.

The swellability of **LPCMP1-NS** was also studied, as shown in Figure S9. Compared with **LPCMP1**, the swelling values of **LPCMP1-NS** are negligible, indicating that the BXJ approach and addition of salt plays an essential role in improving the swelling performance.

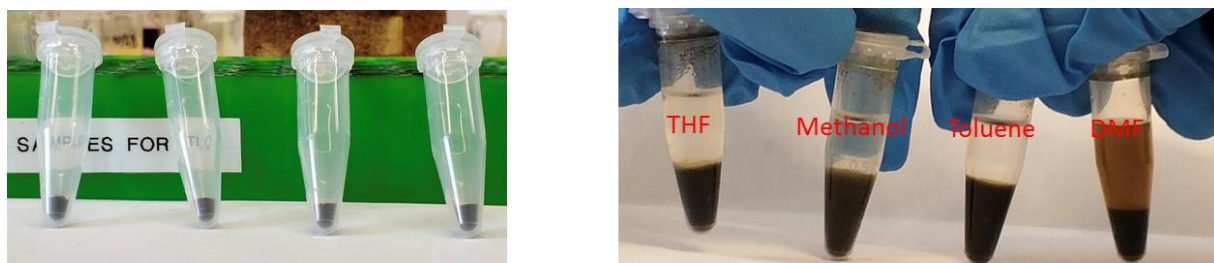


Figure 4. Images of **LPCMP1** before and after swelling with THF, methanol, toluene and DMF, respectively.

Table 3. Swellability (Q) for **LPCMP1-4** against THF, methanol, toluene and DMF.

Sample	Swellability Q (mL g ⁻¹)			
	THF	Methanol	Toluene	DMF
LPCMP1	13.3	16.5	16.0	8.1
LPCMP2	14.5	11.3	11.2	9.8
LPCMP3	16.2	16.2	13.3	9.1
LPCMP4	13.5	11.4	11.7	8.8

Vapor adsorption

The CMPs with high porosity and excellent swellability potentially allow access to the pores for a variety of small vapor molecules. We therefore explored the ability of our CMPs to take up toluene and methanol vapors, as these two volatile organic compounds (VOC) are major air pollutants in the indoor atmosphere.⁴³ Methanol is the simplest of the alcohols, and is used, for example, as a solvent, an alternative fuel, and as feedstock for producing other chemicals.⁴⁴ It is the second most abundant VOC in the atmosphere after methane and promotes the formation of photochemical smog and is also harmful to the nervous system of humans.⁴⁵ Toluene is also a typical VOC pollutant and has been utilized in many chemical manufacturing processes, including as solvent in paints, inks, and in the adhesives industries.⁴⁶ Toluene affects the human nervous system directly, and may lead to acute headaches, dizziness, or unconsciousness.⁴⁷ There is thus a clear need to explore effective adsorbents for methanol and toluene.

Toluene adsorption isotherms of the four obtained polymers at 298 K are shown in **Figure 5**. For **LPCMP2** and **LPCMP4**, Type-I isotherms³⁸ were observed, indicative of monolayer adsorption (i.e., at low pressure, because of the strong interaction between the solid surface of the adsorbent and the vapour adsorbate, the amount adsorbed increases with a rise in pressure). However, after the first adsorbed layer reached saturation, there was no obvious change in the amount of adsorption upon further increasing pressure, indicating the lack of multilayer adsorption. For the **LPCMP1** and **LPCMP3**, Type-IV isotherms³⁸ were observed. Different from the isotherms of **LPCMP2** and **LPCMP4**, after rapid uptake at a low relative pressure,

the adsorption continued to gradually increase with increasing pressure, indicative of multilayer adsorption after saturation of the first adsorbed layer. This behaviour can be explained by the bigger pore size and better swellability of **LPCMP1** and **LPCMP3**. In addition, there is an obvious desorption hysteresis for all four polymers, which is indicative of weak host–guest interactions (π - π stacking), and capillary condensation.³⁸ Owing to the higher specific surface area and better swellability, both **LPCMP1** and **LPCMP3** show excellent vapour adsorption capacity for toluene. The uptake capacities reached 124 wt% and 117 wt%, respectively, at the saturated vapor pressure. The values are comparable with the highest reported toluene adsorption capacity porous materials, such as **CPOP-15** (147 wt%),⁴⁸ **FPOP-1** (98 wt%)⁴⁹ and even **PAF-1** (136 wt%) with an ultrahigh specific surface area.⁵⁰

The methanol adsorption isotherms of the four obtained polymers at 298 K are shown in **Figure 5**. Interestingly, unlike the isotherms for toluene, all four the methanol isotherms are Type-III isotherms, which indicate unrestricted multilayer formation. This behaviour occurs because lateral interactions between adsorbed methanol molecules (hydrogen-bonding interaction) are stronger in comparison to interactions between the adsorbent surface and adsorbate (no π - π stacking interactions).³⁸ Furthermore, negligible hysteresis was detected for all polymers, which, in general, points to a lower required regeneration energy needed for subsequent reuse. The maximum methanol uptake capacities of **LPCMP1** and **LPCMP3** are remarkably high; notably, 250 wt% and 215 wt% for **LPCMP1** and **LPCMP3**, respectively, at methanol saturated vapor pressure. To our knowledge, this adsorption value is the highest recorded when compared with other CMPs, HCPs, MOFs and porous carbons (as shown in Table S2). The previous record for methanol adsorption capacity at 115 wt% was held by **MIL-101(Cr)**, a MOF material for which the BET surface area is significantly higher at 4230 m² g⁻¹. **LPCMP1** and **LPCMP3** show approximately twice the methanol adsorption capacity, despite their surface areas being only approximately one quarter of that determined for **MIL-101(Cr)**.

The outstanding uptake capacity for organic vapors coupled to superior swellability provide very promising application opportunities for these polymers in the area of hazardous organic vapor elimination (including toxic chemical warfare agent uptake and removal).

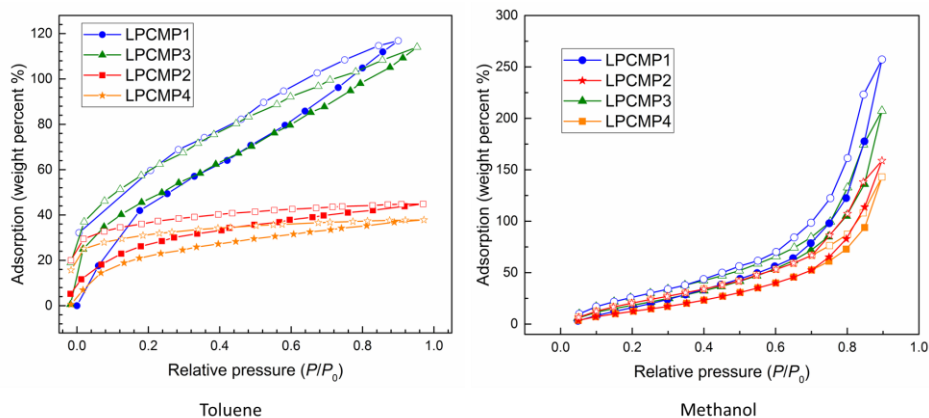


Figure 5. Toluene and methanol adsorption isotherms of **LPCMP1–4** at 298 K (the adsorption and desorption branches are labelled with solid and open symbols, respectively)

Chemical sensing experiments were conducted by adding different concentrations of nitroaromatics (TNT, NP, DNB, DNT, NB) into suspensions of **LPCMP1–4** (10 mg L^{-1}) and monitoring the luminescence quenching. As shown in **Figure 6**, for all the CMPs, the intensity of the fluorescence emission gradually decreased upon increasing the concentration of TNT. Similar fluorescence quenching was observed when NP, DNB, DNT and NB were investigated, but the quenching was less efficient than for TNT. This fluorescence quenching phenomenon can be explained by a donor–acceptor electron-transfer mechanism. When nitroaromatics are added to the CMP suspensions π -stacking interactions occur between the conjugated networks of the CMPs and the nitroaromatics. Upon excitation, electrons are transferred from the CMPs’ conduction band to the lowest unoccupied molecular orbital (LUMO) of the nitroaromatics, which results in the observed quenching.¹⁵

In order to quantify the quenching efficiencies of the different CMPs for different nitroaromatics, the Stern–Volmer equation ($I_0 / I = K_{sv} [C]$, with I_0 the initial fluorescence

intensity, I the fluorescence intensity measured at different concentration of nitroaromatics and K_{sv} the Stern–Volmer constant) was applied. The Stern–Volmer plots for all CMPs are shown in **Figure 7**. The Stern–Volmer plots show a strong linear relationship between the I_0 / I and the concentration of nitroaromatics. Moreover, the quenching efficiencies can be quantified by the slope (K_{sv}) of the lines. For all the CMPs, TNT gives the highest quenching efficiencies, with descending quenching efficiency: TNT > NP > DB > DT > NB. The LUMO levels of all the nitroaromatics were also calculated using the density functional theory (DFT) calculations which were performed with the GaussView 5.0 and MobaXterm software, using the B3LYP functional and the 6-31G(d) basis set. The LUMO energy level order from low to high is TNT < NP < DB < DT < NB, which matches the quenching efficiency exactly. This trend indicates that excited electrons from the CMP networks can be transferred to the LUMO of TNT with highest efficiency, with the obtained results in accordance with the quenching efficiency order. It should be mentioned that the Stern–Volmer constants (K_{sv}) of **LPCMP2** and **LPCMP3** for TNT (4147 and 1245 M^{-1} , respectively), which are comparable to other reported CMPs chemosensors,⁵¹ are one order of magnitude higher than for the other nitroaromatics. This result indicates that both **LPCMP2** and **LPCMP4** exhibit high selectivity for TNT and may be suitable as new candidates to selectively detect TNT for security or environmental applications.

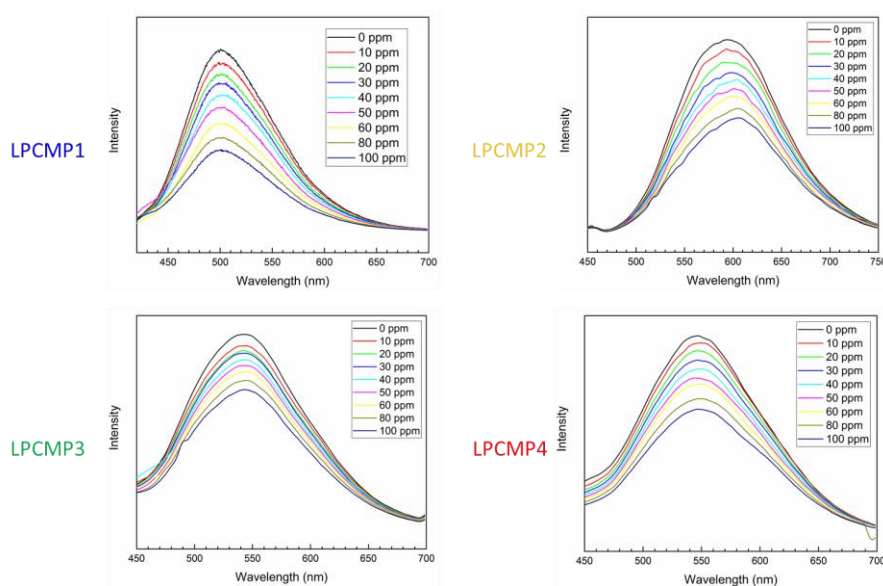


Figure 6. Photoluminescence quenching of LPCMP1-4 with various concentrations of TNT (for **LPCMP1, 2** $\lambda_{ex} = 380$ nm for **LPCMP3, 4** $\lambda_{ex} = 400$ nm)

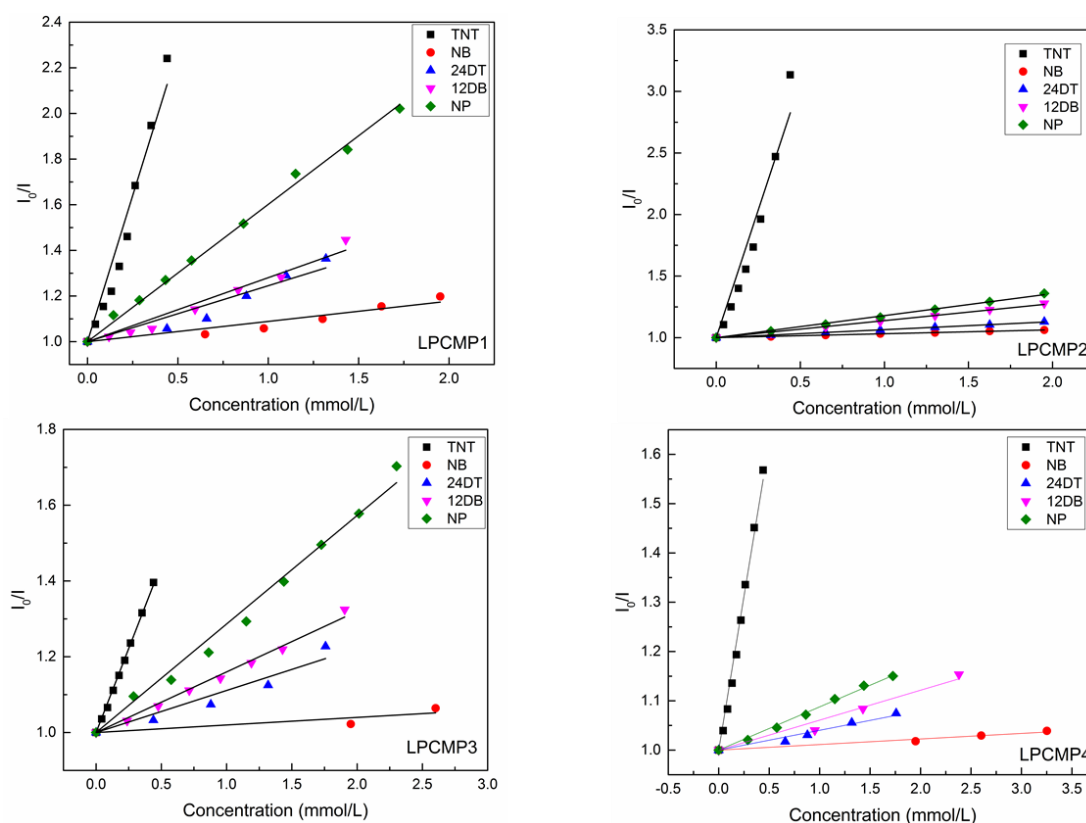


Figure 7. Stern–Volmer plots of **LPCMP1-4**

Table 4. K_{sv} value of **LPCMP1-4** for the different nitroaromatics

Material	K_{sv} (M^{-1})				
	TNT	NP	DB	DT	NB
LPCMP1	2563	602	283	245	89
LPCMP2	4147	179	138	65	32
LPCMP3	886	286	163	111	20
LPCMP4	1245	88	61	40	11

Conclusions

In conclusion, four new conjugated microporous polymers were synthesised by BH cross coupling reaction. The surface areas and pore size distributions of the polymers were tuned by changing the chemical structure of the building blocks, varying the ratios of bromine and amine

building blocks and application of our recently developed BXJ method. The produced CMP materials possess not only high Brunauer–Emmett–Teller (BET) specific surface areas, high chemical and thermal stabilities, but also exhibit strong luminescence. They show very sensitive and selective fluorescence quenching in the presence of trace amount of nitroaromatic compounds. In terms of environmental and security concerns, the present study suggests that these materials may be used as fluorescent sensors for nitroaromatics. Moreover, all the CMPs show outstanding ability to take up large volumes of organic liquids (including toluene, tetrahydrofuran (THF) and methanol) by swelling of the porous networks. As far as we know, no other CMPs have been shown to possess this unique property, which could be utilised in environmental and related applications. Owing to their excellent swellability, we further studied the adsorption capacity of the CMPs for different toxic volatile organic vapours, specifically toluene and methanol. Impressively, **LPCMP1** and **LPCM3** exhibit excellent toluene adsorption capacity, while they possess the highest methanol adsorption capacity by a factor of two when compared with the best published data. These materials show great potential for application in indoor air quality remediation, general hazardous organic vapour elimination and chemical warfare agent uptake – wide application of our materials is envisaged.

Acknowledgements

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