Microporous, Tetraarylethylene-based Polymer Networks generated in a Reductive Polyolefination Process

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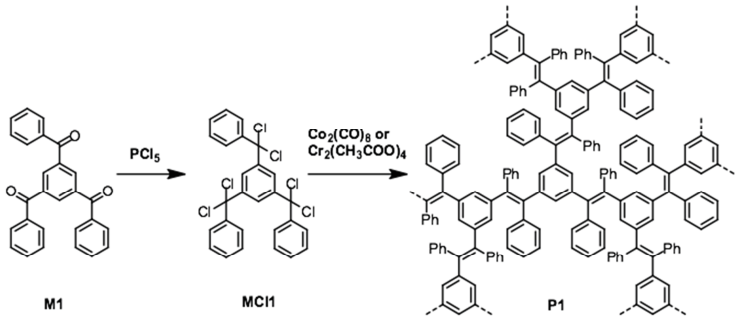
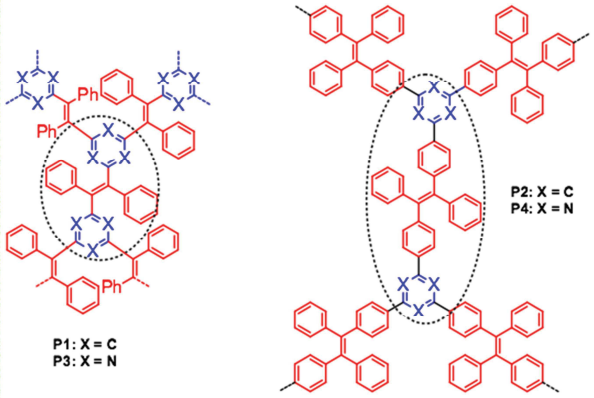
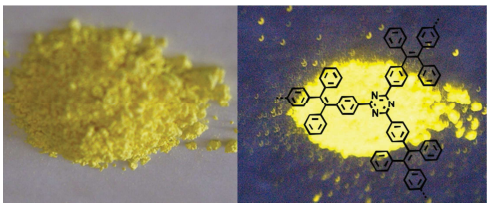
Introduction

Microporous Polymer Networks (MPNs) comprise a rapidly growing area of materials science towards future mass applications in catalysis, gas storage/separation or as active porous materials for organic electronic devices and sensors [1-7].

MPNs that contain aggregate-induced emission (AIE)-active tetraphenylethylene (TPE) or other tetraarylethylene units have been generated in a reductive polyolefination process starting from four different tris(⟨ ,⟨ -dichlorobenzyl)arene derivatives with dicobalt octacarbonyl or chromium(II) acetate as reductive olefination agents. Microporosity with moderately high BET surface areas up to 500 m²/g could be combined with high solid state photoluminescence quantum yields up to 25.3 %.







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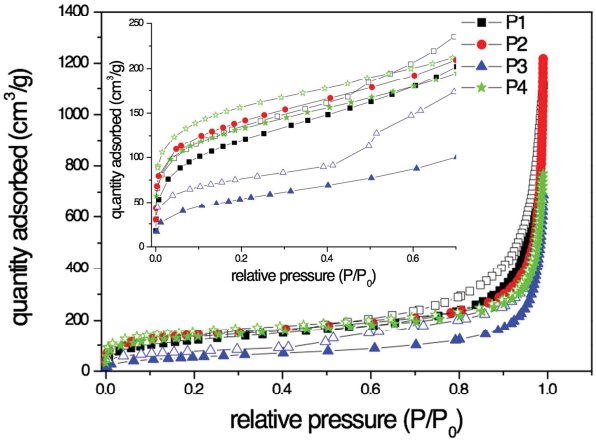
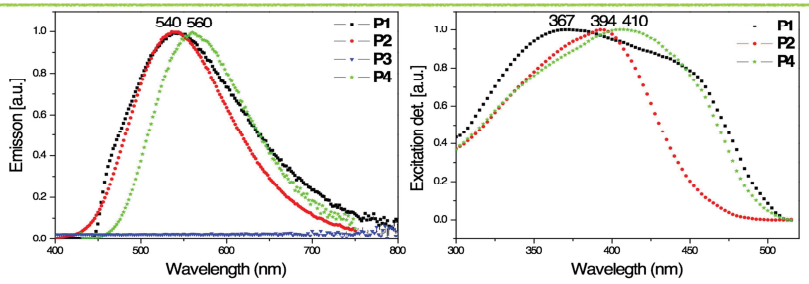
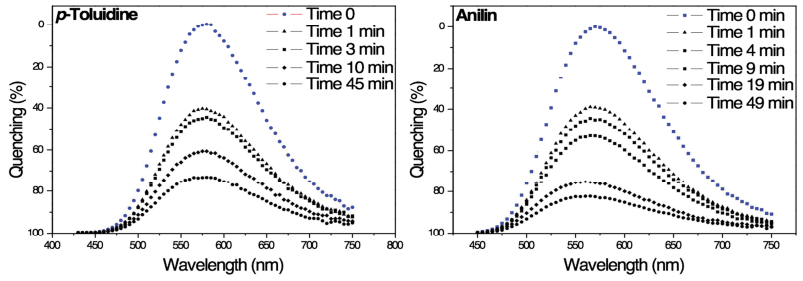


Nitrogen adsorption (*filled symbols*)/desorption (*open symbols*) isotherms at 77 K for P1 (*black squares*), P2 (*red circles*), P3 (*blue triangles*), P4 (*green stars*); the inset shows the pressure range P/P_0 from 0 to 0.7.



PL spectra (l_{exc} = 400 nm) (left) and PL excitation spectra (l_{det} = 550 nm) (right) of P1 (black square), P2 (red circle), P3 (blue triangle), P4 (green star).



PL quenching experiments with P4 pellets and *p*-toluidine or aniline as analytes.

	BET surface area (m^2/g)	Pore volume (cc)	H_2 uptake (%)	CO_2 uptake (%)	CH_4 uptake (%)	Selectivity (CO_2/CH_4) (298 K)	Selectivity (N_2/H_2) (77 K)
P1	***462***	***1.76***	***0.44***	***1.46***	***0.11***	***4.7***	***24.2***
P2	502	1.87	0.57	2.54	0.26	3.6	19.3
P3	***200***	***1.05***	***0.35***	***1.58***	***0.12***	***4.6***	***18.0***
P4	475	1.16	0.55	2.58	0.26	3.6	12.6

	UV/Vis (λ_{max}, nm)	PL (λ_{max}, nm)	PLQY (%)	First decomposition step (TGA, under argon, °C)
P1	***352***	***540***	***3.5***	***272 (2.5 %)***
P2	363	540	6.5	386 (2.6 %)
P3	***367***	***no PL detected***	***-***	***296 (7.9 %)***
P4	392	560	25.3	408 (1.5 %)

Conclusion

- Novel microporous polymer networks P1-P4 have been successfully synthesized via a reductive polyolefination protocol.
- Polymer network P4 shows an intense yellow photoluminescence peaking at 560 nm with a remarkably high PLQY of 25.3 % .
- Intrinsic microporosity with a moderately high BET surface area up to 500 m²/g was determined.
- Combination of microporosity and high solid state PLQY (based on the AIE effect) clearly qualifies P4 as an attractive target for solid state sensing.
- Notably, orienting PL quenching experiments have demonstrated a distinct response to aromatic amine vapors (showed for aniline and *p*-toluidine).

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