Rationalising the Influence of Solvent Choice on the Porosity of Conjugated Microporous Polymers

Supporting Information

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- 1. Catalytic formation cycle.
- 2. Microporous surface areas of the CMP networks
- 3. Solvent structure and polarity indices
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Figure S1: Sonogashira-Hagihara catalytic cycle for the reaction of TEB with an aromatic DBM.

Table S1: Microporous surface area for CMP networks prepared using DMF, toluene, THF and1,4-dioxane as reaction solvents.

СМР	Microporous surface area of the CMP network / m ² g ⁻¹				
network	DMF	Toluene	THF	1,4-Dioxane	
1	594	286	273	390	
2	394	43	301	394	
3	314		193	212	
4	297	182	198	191	
5	311	270	229	191	
6	584	122	407	381	
7	405	164	345	460	
8	693	359	390	556	
9	377	96	255	551	
10	451	114	388	299	
11	594	164	395	276	

Solvent	Molecular Structure	Polarity Index
DMF	O N CH ₃ CH ₃	6.4
Toluene	CH3	2.4
THF	\sim	4.0
1,4-Dioxane		4.8

Table S2: Polarity indices of each of the solvents studied in this work. Also given is the molecular structure of each solvent.⁸

Table S3: Absolute difference in the dipole moment of each DBM relative to TEB, for the CMP reagents presented here.

Manamar	Mulliken Dipole Moment /	Absolute difference in dipole
wonomer	Debye	moment relative to TEB / Debye
1	0.0001	0.0001
2	0.0002	0.0000
3	0.0003	0.0001
4	0.7045	0.7043
5	0.0000	0.0002
6	0.0017	0.0015
7	0.0000	0.0002
8	0.0001	0.0001
9	4.1278	4.1276
10	0.3503	0.3501
11	3.1943	3.1941
TEB	0.0002	0.0000



Figure S2a: Plot of the microporous surface area of CMP networks 1-11 against the polarity index of the reaction solvent.^{7,8} Key: CMP-1 – blue, CMP-2 – orange, CMP-3 – pink, CMP-4 – black, CMP-5 – purple, CMP-6 – green, CMP-7 – red, CMP-8 – brown, CMP-9 – grey, CMP-10 – burgundy (dark red), CMP-11 – dark blue. Solvent polarity indices: DMF – 6.4, 1,4-Dioxane – 4.8, THF – 4.0, Toluene – 2.4 (shown as grey dashed lines on the graph for clarity).



Figure S2b: Plot of the microporous surface area of CMP network 1 against the polarity index of the reaction solvent.^{7,8} Solvent polarity indices: DMF - 6.4, 1,4-Dioxane - 4.8, THF - 4.0, Toluene - 2.4 (shown as grey dashed lines on the graph for clarity).



Figure S2c: Plot of the microporous surface area of CMP network 2 against the polarity index of the reaction solvent.^{7,8} Solvent polarity indices: DMF – 6.4, 1,4-Dioxane – 4.8, THF – 4.0, Toluene – 2.4 (shown as grey dashed lines on the graph for clarity).



Figure S2d: Plot of the microporous surface area of CMP network 3 against the polarity index of the reaction solvent.^{7,8} Solvent polarity indices: DMF – 6.4, 1,4-Dioxane – 4.8, THF – 4.0, Toluene – 2.4 (shown as grey dashed lines on the graph for clarity).



Figure S2e: Plot of the microporous surface area of CMP network 5 against the polarity index of the reaction solvent.^{7,8} Solvent polarity indices: DMF – 6.4, 1,4-Dioxane – 4.8, THF – 4.0, Toluene – 2.4 (shown as grey dashed lines on the graph for clarity).



Figure S2f: Plot of the microporous surface area of CMP network 6 against the polarity index of the reaction solvent.^{7,8} Solvent polarity indices: DMF – 6.4, 1,4-Dioxane – 4.8, THF – 4.0, Toluene – 2.4 (shown as grey dashed lines on the graph for clarity).



Figure S2g: Plot of the microporous surface area of CMP network 7 against the polarity index of the reaction solvent.^{7,8} Solvent polarity indices: DMF – 6.4, 1,4-Dioxane – 4.8, THF – 4.0, Toluene – 2.4 (shown as grey dashed lines on the graph for clarity).



Figure S2h: Plot of the microporous surface area of CMP network 8 against the polarity index of the reaction solvent.^{7,8} Solvent polarity indices: DMF – 6.4, 1,4-Dioxane – 4.8, THF – 4.0, Toluene – 2.4 (shown as grey dashed lines on the graph for clarity).



Figure S2i: Plot of the microporous surface area of CMP network 10 against the polarity index of the reaction solvent.^{7,8} Solvent polarity indices: DMF – 6.4, 1,4-Dioxane – 4.8, THF – 4.0, Toluene – 2.4 (shown as grey dashed lines on the graph for clarity).



Figure S2j: Plot of the microporous surface area of CMP network 11 against the polarity index of the reaction solvent.^{7,8} Solvent polarity indices: DMF – 6.4, 1,4-Dioxane – 4.8, THF – 4.0, Toluene – 2.4 (shown as grey dashed lines on the graph for clarity).