Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Exploring the effect of molecular size and framework functionalisation on transport in metal-organic frameworks using pulsed-field gradient nuclear magnetic resonance

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Electronic Supplementary Information (ESI)

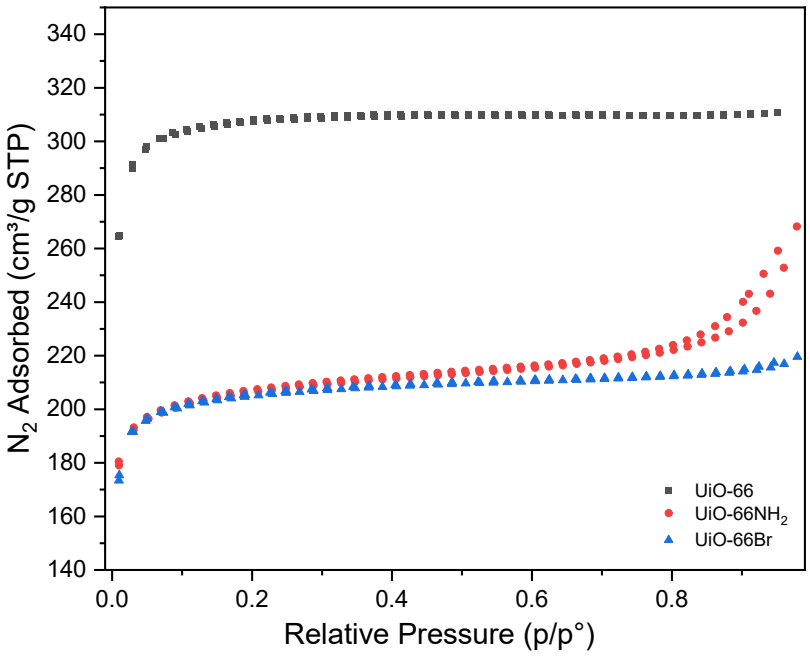

Figure S1. N_2 adsorption-desorption isotherms for UiO66 and its derivatives at 77 K.

Table S1. Textural properties and calculated pore sizes of the MOFs under investigation.

MOF	**Surface area (*SA*)** $(m^2g^{-1})^a$	**Pore diameter (d_{XRD})** **(nm)**[b]	**Pore volume (*V*)** $(cm^3g^{-1})^c$
UiO-66	953	0.8, 1.4	0.45
UiO-66NH_2	892	0.8, 1.4	0.27
UiO-66Br	691	0.8, 1.4	0.28

[a] By the BET method using the N_2 physisorption isotherms; [b] Estimated pore sizes based on CIF file; [c] t-plot

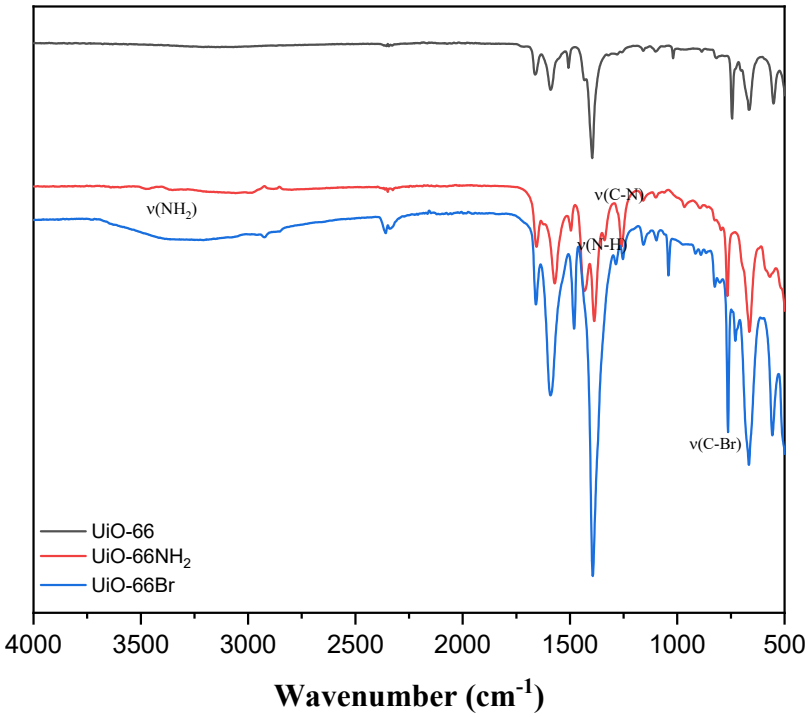

Figure S2. FT-IR spectra of the pristine UiO-66 MOF and its derivatives.

Table S2. Characteristic IR bands of the linkers and MOFs under investigation.

Compound	**Colour**	***ν* (C-NH_2) (cm^{-1})**	***ν* (C-N) (cm^{-1})**	***ν* (C-Br) (cm^{-1})**	***ν* (C=O) (cm^{-1})**	**ν (OH) (cm^{-1})**
BDC	White	-	-	-	1700 (s)	2900 (m)
NH_2-BDC	Yellow	3507 (m) 3384 (m)	1210 (m)	-	1705 (s)	2901(m)
Br-BDC	White	-	-	680 (m)	1710 (s)	2914 (m)
UiO-66	White					
UiO-66NH_2	Yellow	3501 (br) 3390 (br)	1250 (m)			
UiO-66Br	White			690 (m)		

br = broad; s = strong; m = medium.

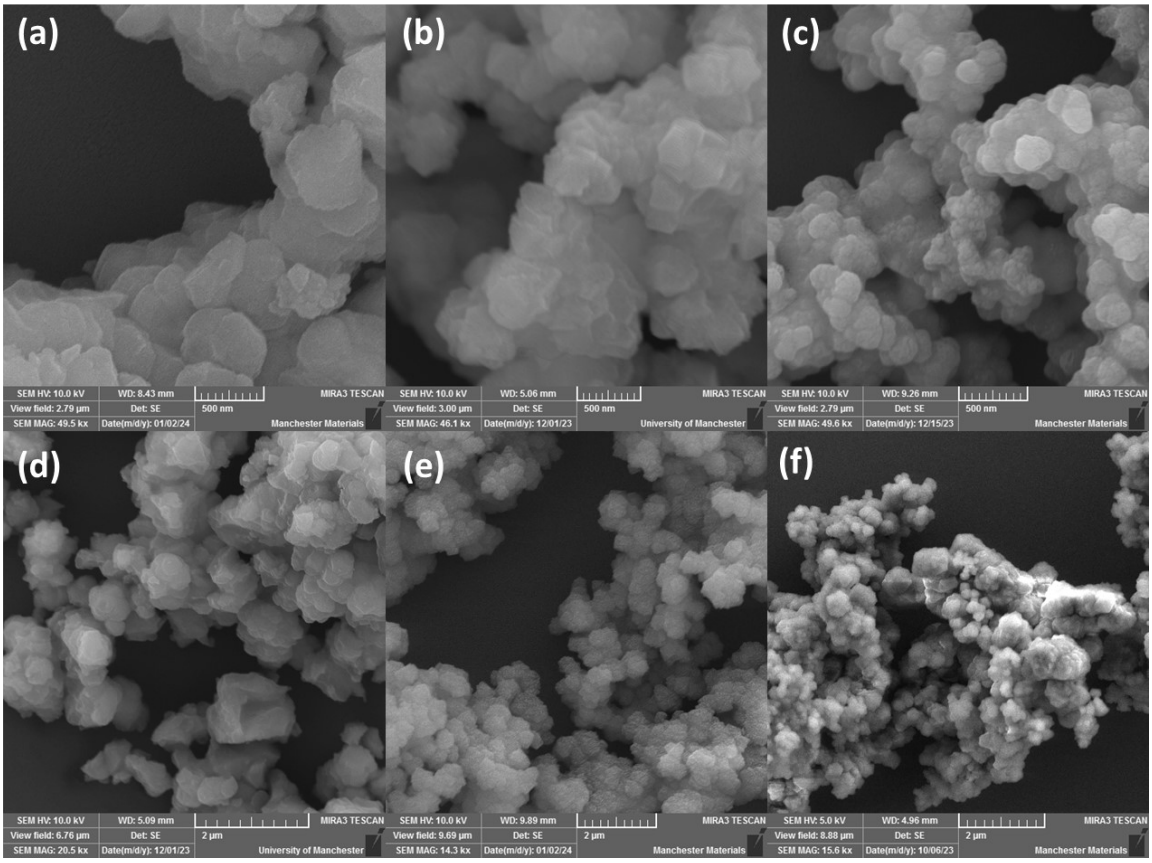

Figure S3. SEM images for (a)(d) UiO-66, (b)(e) UiO-66NH_2 and (c)(f) UiO-66Br at 500 nm and 2 μm, respectively.

Table S3. Summary of the diffusion results for water, *p*-xylene, *m*-xylene, *o*-xylene, *n*-octane and TIPB in UiO-66 at an observation time Δ = 100 ms. $D_{1,self}$ represents the fast diffusion coefficient, while $D_{2,self}$ represents the slow diffusion coefficient.

Probe molecule	D_{bulk} (10^{-10} m^2 s^{-1})	$D_{1,self}$ (10^{-10} m^2 s^{-1})	$D_{2,self}$ (10^{-10} m^2 s^{-1})	$\xi_1 = \frac{D_{bulk}}{D_{1,self}}$	$\xi_2 = \frac{D_{bulk}}{D_{2,self}}$	$RMSD_1$ (μm)	$RMSD_2$ (μm)
Water	23.3 ± 0.03	10.9 ± 0.10	1.13 ± 0.31	2.13 ± 0.15	20.6 ± 1.44	14.7	4.75
p-Xylene	21.2 ± 0.02	12.6 ± 0.22	2.30 ± 0.08	1.68 ± 0.12	9.22 ± 0.65	15.9	6.78
m-Xylene	20.2 ± 0.02	12.5 ± 0.23	1.91 ± 0.12	1.62 ± 0.11	10.6 ± 0.74	15.8	6.18
o-Xylene	16.0 ± 0.02	9.93 ± 0.21	1.41 ± 0.07	1.61 ± 0.11	11.3 ± 0.79	14.1	5.31
n-Octane	23.6 ± 0.03	10.5 ± 0.33	1.47 ± 0.07	2.25 ± 0.15	16.1 ± 1.13	14.5	5.42
TIPB	2.45 ± 0.01	1.78 ± 0.01	-	1.38 ± 0.09	-	5.97	-

Table S4. Summary of the diffusion results of water, *p*-xylene, *m*-xylene, *o*-xylene, *n*-octane and TIPB in UiO-66NH_2 at an observation time Δ = 100 ms. $D_{1,self}$ represents the fast diffusion coefficient, while $D_{2,self}$ represents the slow diffusion coefficient.

Probe molecule	D_{bulk} (10^{-10} $m^2 s^{-1}$)	$D_{1,self}$ (10^{-10} $m^2 s^{-1}$)	$D_{2,self}$ (10^{-10} $m^2 s^{-1}$)	$\xi_1 = \frac{D_{bulk}}{D_{,1self}}$	$\xi_2 = \frac{D_{bulk}}{D_{2,self}}$	$RMSD_1$ (μm)	$RMSD_2$ (μm)
Water	23.3 ± 0.03	9.72 ± 0.31	0.26 ± 0.31	2.40 ± 0.17	89.6 ± 6.27	13.9	2.28
p-Xylene	21.2 ± 0.02	12.4 ± 0.11	1.83 ± 0.17	1.71 ± 0.12	11.6 ± 0.81	15.7	6.05
m-Xylene	20.2 ± 0.02	12.5 ± 0.11	1.72 ± 0.19	1.62 ± 0.11	11.7 ± 0.82	15.8	5.87
o-Xylene	16.0 ± 0.02	9.73 ± 0.06	1.66 ± 0.10	1.64 ± 0.12	9.64 ± 0.67	13.9	5.76
n-Octane	23.6 ± 0.03	12.4 ± 0.13	0.45 ± 0.03	1.90 ± 0.13	52.4 ± 3.67	15.7	3.00
TIPB	2.45 ± 0.01	1.84 ± 0.01	-	1.33 ± 0.09	-	6.06	-

Table S5. Summary of the diffusion results of water, *p*-xylene, *m*-xylene, *o*-xylene, *n*-octane and TIPB in UiO-66Br at an observation time Δ = 100 ms. $D_{1,self}$ represents the fast diffusion coefficient, while $D_{2,self}$ represents the slow diffusion coefficient.

Probe molecule	D_{bulk} (10^{-10} $m^2 s^{-1}$)	$D_{1,self}$ (10^{-10} $m^2 s^{-1}$)	$D_{2,self}$ (10^{-10} $m^2 s^{-1}$)	$\xi_1 = \frac{D_{bulk}}{D_{1,self}}$	$\xi_2 = \frac{D_{bulk}}{D_{2,self}}$	$RMSD_1$ (μm)	$RMSD_2$ (μm)
Water	23.3 ± 0.03	12.5 ± 0.07	1.79 ± 0.30	1.86 ± 0.13	13.2 ± 0.92	15.8	5.98
p-Xylene	21.2 ± 0.02	14.9 ± 0.07	2.42 ± 0.19	1.42 ± 0.10	8.76 ± 0.61	17.3	6.96
m-Xylene	20.2 ± 0.02	12.6 ± 0.12	1.35 ± 0.14	1.60 ± 0.11	14.9 ± 1.04	15.8	5.20
o-Xylene	16.0 ± 0.02	11.4 ± 0.03	1.28 ± 0.16	1.40 ± 0.10	12.5 ± 0.88	15.1	4.75
n-Octane	23.6 ± 0.03	16.1 ± 0.10	1.13 ± 0.21	1.47 ± 0.10	20.6 ± 1.44	17.9	4.52
TIPB	2.45 ± 0.01	1.75 ± 0.01	-	1.40 ± 0.10	-	5.92	-

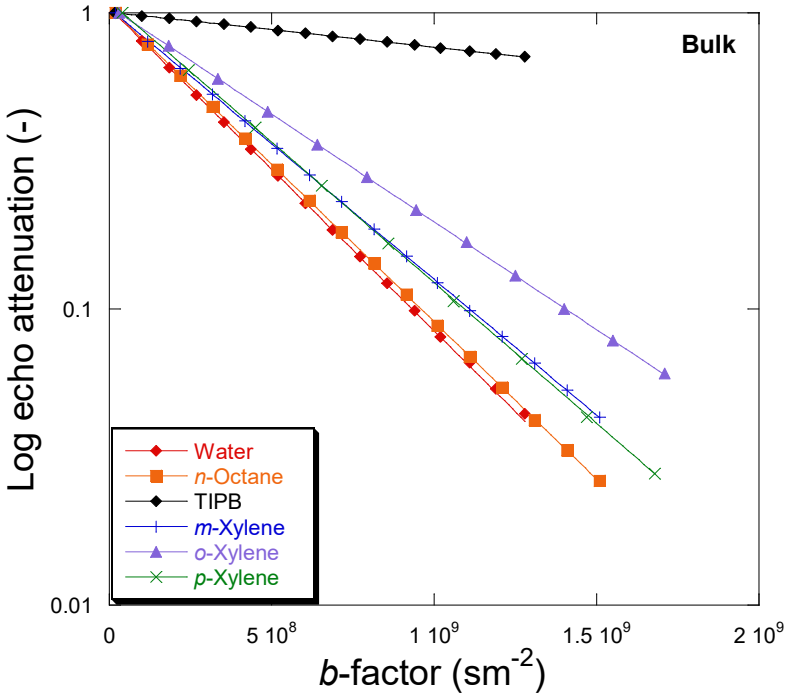

Figure S4. Diffusion attenuation plots for all bulk probe molecules.

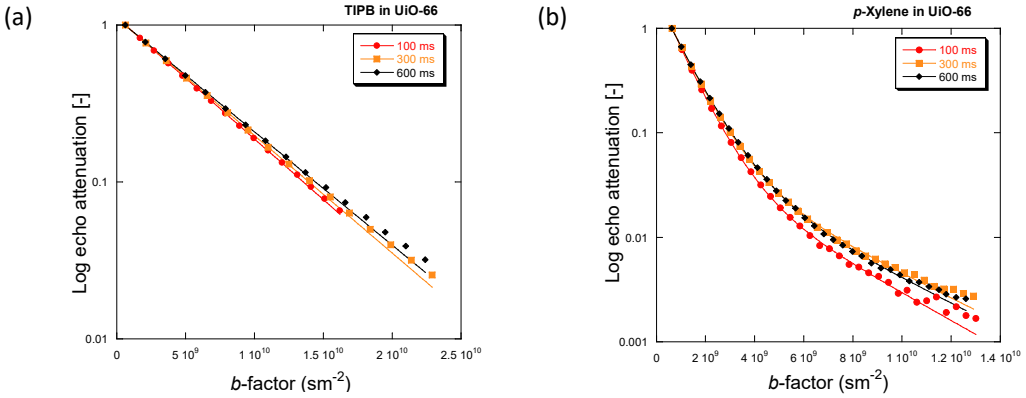

Figure S5. Diffusion attenuation plots for (a)TIPB and (b) *p*-xylene within the porous network of UiO-66 at different diffusion observation times.

Table S6. Summary of the diffusion results of all probe molecules in UiO-66 at different observation time Δ. $D_{1,self}$ represents the first diffusion coefficient, while $D_{2,self}$ represents the second self-diffusion coefficient.

	Observation time Δ [ms]					
	100		**300**		**600**	
Probe molecule	$D_{1,self}$ (10^{-10} $m^2 s^{-1}$)	$D_{2,self}$ (10^{-10} $m^2 s^{-1}$)	$D_{1,self}$ (10^{-10} $m^2 s^{-1}$)	$D_{2,self}$ (10^{-10} $m^2 s^{-1}$)	$D_{1,self}$ (10^{-10} $m^2 s^{-1}$)	$D_{2,self}$ (10^{-10} $m^2 s^{-1}$)
TIPB	1.8 ± 0.02	-	1.8 ± 0.02	-	1.7 ± 0.01	-
p-Xylene	12.6 ± 0.22	2.3 ± 0.08	10.8 ± 0.02	2.1 ± 0.02	10.5 ± 0.01	2.2 ± 0.04