

SUPPORTING INFORMATION

Crystal-to-Cocrystal Transformation as a Novel Approach for the Removal of Aromatic Sulfur Compounds from Fuels

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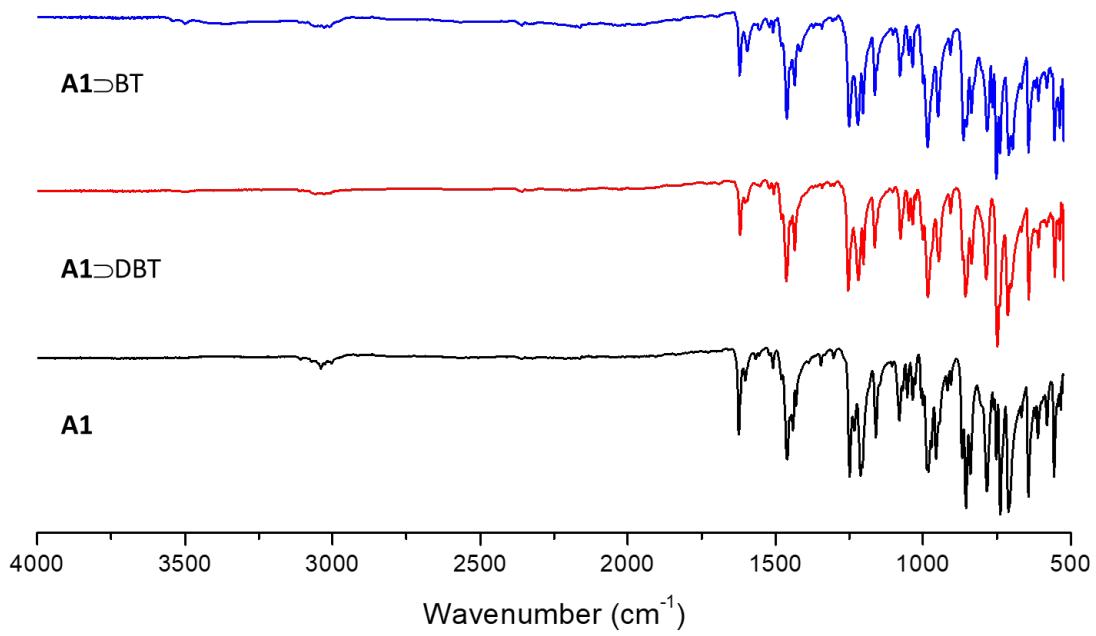


Figure S1. FT-IR spectra of **A1-DBT**, **A1-DBT** and **A1**.

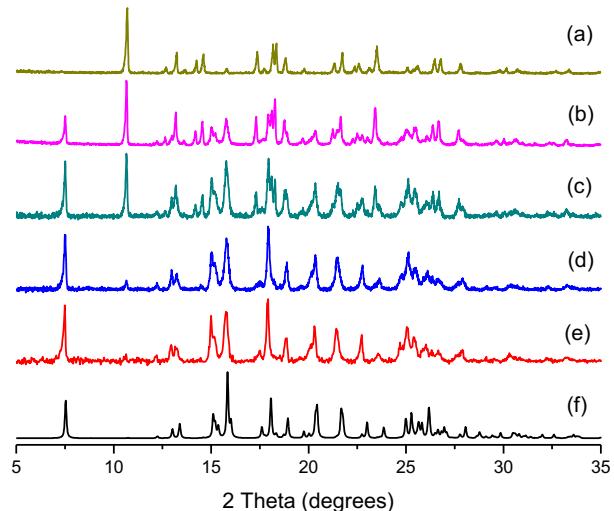


Figure S2. PXRD patterns of (a) **A1**; (b)-(e) the solids recollected after DBT uptake from a cyclohexane solution containing 1000 ppmwS; 1500 ppmwS; 2000 ppmwS; 3000 ppmwS (from top to bottom); and (f) **A1-DBT** (simulated from scXRD analysis).

Table S1. Performance of adsorbents commonly used in desulfurization of DBT.

Sample	Adsorbent type	Solvent	Adsorption capacity (mmol S per g)	Reference
A1	C-to-CC	Cyclohexane	1.45±0.05	This work
A1	C-to-CC	n-Hexane	1.33±0.03	This work
A1	C-to-CC	i-octane	1.34±0.04	This work
BPS	AC	n-Hexane	2.56	1
PS	AC	n-Hexane	2.03	1
C-700	AC	n-Hexane	1.54	2
ACF	AC	n-Hexane	1.46	3
GCSAC	AC	n-Hexane	1.26	3
Sn-AC	AC	Cyclohexane ^a	0.45	4
MIP-GO	MIP	n-Hexane	0.99	5
SMIP-AC	MIP	n-Hexane	0.65	6
Fe ₃ O ₄ @mSiO ₂ @DT-MIP	MIP	n-Hexane	0.56	7
CMSs-MIP	MIP	n-Hexane	0.48	8
UMCM-153	MOF	n-Octane	2.78	9
UMCM-150	MOF	i-octane	2.59	10
PCN	MOF	i-octane	2.35	11
UMCM-152	MOF	n-Octane	1.84	9
IFMC-16	MOF	i-octane	1.56	12
HKUST-1	MOF	i-octane	1.40	10
MOF-505	MOF	i-octane	1.22	10
CPO-27(Co)	MOF	Heptane/toluene	1.08	13
CPO-27(Ni)	MOF	Heptane/toluene	1.08	13
MOF-5	MOF	i-octane	1.07	10
Ag(I)Y	Zeolite	n-Octane ^a	0.54	14
Cu(II)Zn(II)Y	Zeolite	n-Octane ^a	0.54	14
Zn(II)Y	Zeolite	n-Octane ^a	0.47	14
Ni(II)Ce(IV)Y	Zeolite	n-Octane	0.24	15
Beta-40	Zeolite	Cyclohexane	0.05	16
Meso-Cu/SiO ₂	MS	n-Octane	1.09	17
Ni/Al-KIT-6	MS	n-Octane	0.69	18
Ag/Al-MCM-41	MS	n-Decane	0.47	19
Ag-MSN	MS	n-Decane	0.40	20

C-to-CC: Crystal-to-Cocrystal. AC: activated carbon; MIP: molecular imprinted polymer; MOF: metal organic framework; MS: mesoporous silica. Experimental conditions include batch adsorption experiments at 25 °C and atmospheric pressures, unless otherwise cited. [a] 60°C.

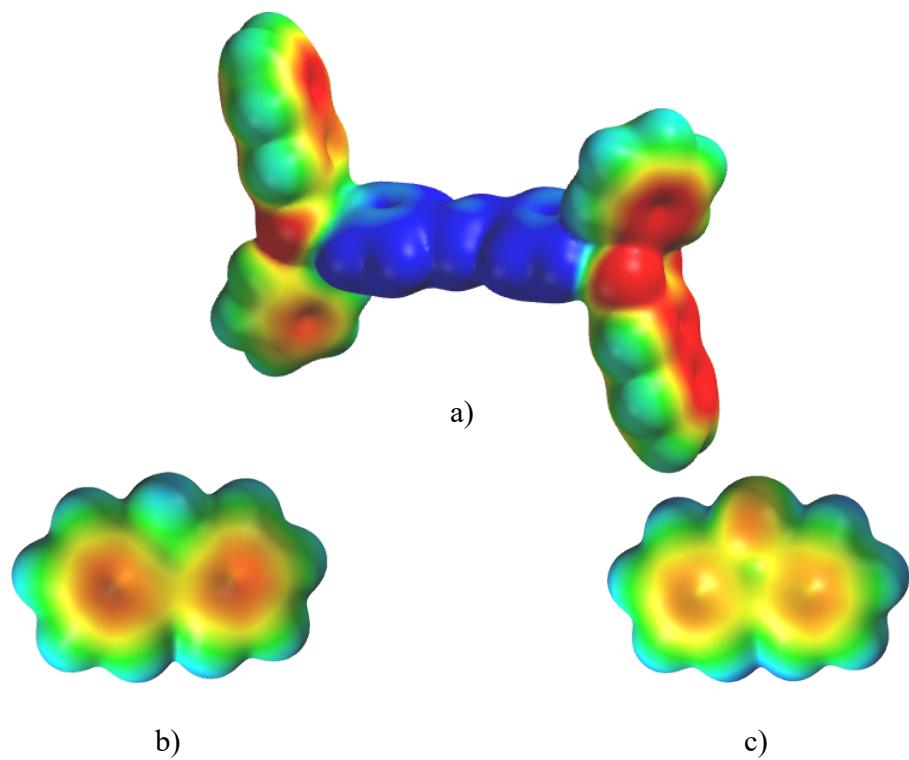


Figure S3. Electrostatic potential surfaces of a) **A1**, b) fluorene (FLUO) and c) dibenzothiophene (DBT).²¹

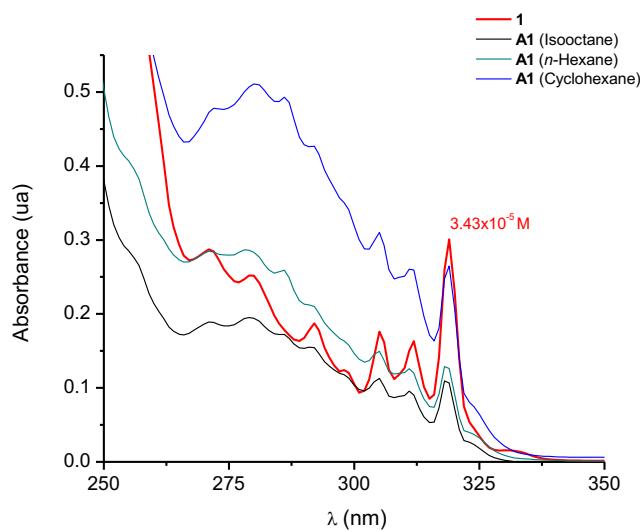


Figure S4. UV absorption spectrum of boronic ester **1** at a concentration of 3.4×10^{-5} M in cyclohexane (red line). UV absorption spectra of the solutions obtained after stirring 0.1 g of **A1** for 12 hours at 25°C in *i*-octane (7.2×10^{-6} M of **A1** according to the calibration curve measured at 319 nm for **1**), *n*-hexane (8.1×10^{-6} M of **A1** according to the calibration curve measured at 319 nm for **1**) and cyclohexane (1.5×10^{-5} M of **A1** according to the calibration curve measured at 319 nm for **1**).

Table S2. Solubility and maximum percentage of **A1** dissolved in cyclohexane, *n*-hexane and *i*-octane.^a

Solvent	Concentration of 1 in solution (M)	Amount of A1 in 3mL (mg)	Weight percentage (%)
Cyclohexane	3.01×10^{-5}	0.030	0.030
<i>n</i> -Hexane	1.63×10^{-5}	0.016	0.016
<i>i</i> -octane	1.43×10^{-5}	0.014	0.014

^a Experimental conditions: 100 mg of **A1** in 3 mL of the solvent (cyclohexane, *n*-hexane or *i*-octane) were stirred at 25 °C during 12 h. After this time, the sample was filtered and the amount of **A1** in solution was quantified by UV-vis spectroscopy using calibration curves at 319 nm (see Figure S4).

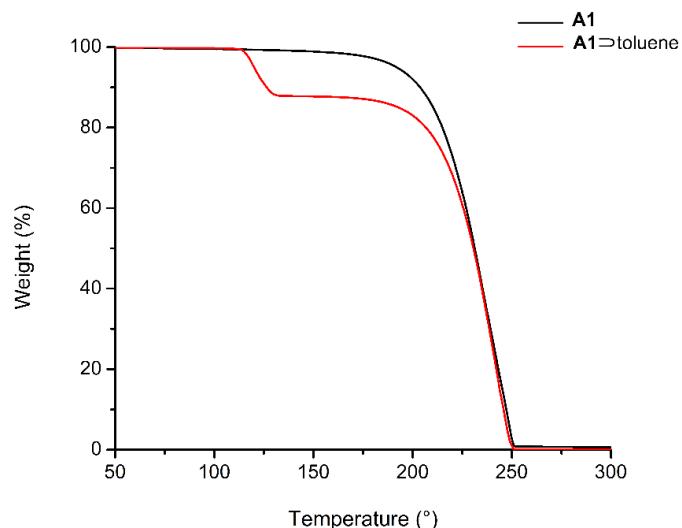


Figure S5. Thermogravimetric analysis of **A1** and **A1**–toluene (weight loss exp.:12.09%; calcd.: 12.02%, corresponding to one toluene molecule).

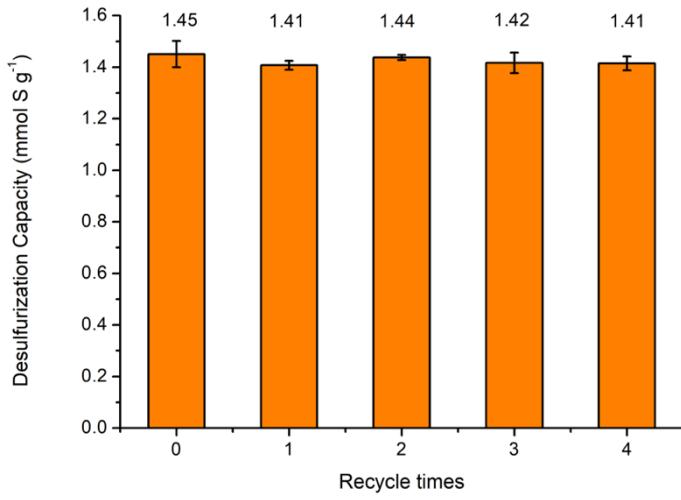


Figure S6. DBT uptake performance of **A1** after four regeneration cycles ($C_0 = 3000$ ppmwS, exposure time 12 h, $T = 25$ °C, $n = 3 \pm \text{SD}$).

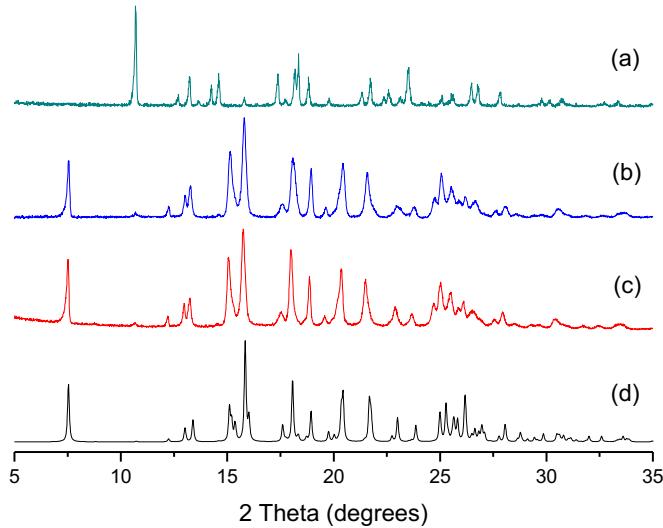


Figure S7. PXRD patterns for (a) pristine **A1**; (b) solid recollected from desulfurization experiments using an equimolar five-component solution of BT, DBT, DMDBT, NAPH and FLUO (0.075 mmol each, corresponding to five molar equivalents of guest per **A1**) after addition of 0.05 g of **A1** (0.075 mmol, exposure time 12 h at 25 °C); (c) solid recollected from a similar experiment but using 0.10 g of **A1** (0.150 mmol); and (d) **A1**⊃DBT. (simulated from scXRD data).

Table S3. Composition of the solid (in percentage %) recollected after desulfurization experiments using an equimolar solution of BT, DBT, DMDBT, NAPH and FLUO (0.025 M each, 0.075 mmol each) by one (0.05 g, 0.075 mmol) and two (0.10 g, 0.150 mmol) equivalents of **A1** after 12 h of exposure time at 25 °C.^a

compound	Composition of the solid (%)	
	0.075 mmol of A1	0.150 mmol of A1
A1 ▷BT	6.1 ± 0.2	9.2 ± 0.6
A1 ▷DBT	56.8 ± 2.5	40.7 ± 2.6
A1 ▷DMDBT	3.5 ± 0.2	4.3 ± 0.4
A1 ▷NAPH	11.5 ± 0.2	17.7 ± 1.2
A1 ▷FLUO	17.5 ± 0.7	22.3 ± 1.5
TOTAL	95.4 ± 3.8	94.2 ± 6.3

^a Concentration of sulfur and non-sulfur compounds removed from the fuel mixture by **A1** was quantified by dissolving the resultant solids in methanol and evaluating the concentration of each compound by HPLC-UV.

Table S4. Percentage of removal of BT, DBT, DMDBT, NAPH and FLUO by **A1** from single-component solutions after different stirring time intervals.^a

Time (h)	BT	DBT	DMDBT	NAPH	FLUO
0.5	2.6	4.7	2.6	0	5.4
1	2.0	36.9	1.7	2.0	6.9
2	2.0	84.0	1.1	12.2	9.6
4	2.0	92.3	1.4	35.9	12.4
6	3.4	93.3	3.2	53.1	16.0
8	6.3	93.5	2.2	63.6	17.9
12	8.9	93.1	2.7	68.4	24.6

^a Each compound was quantified by UV-vis spectroscopy using calibration curves at the following wavelengths:
BT (297 nm), DBT (326 nm), DMDBT (326 nm), NAPH (286 nm), and FLUO (301 nm).

Table S5. Relevant physical properties of the aromatic guest employed (BT, DBT, DMBT, NAPH and FLUO).^a

Guest	Area ^b	Log P ^c	Δ _{sub} H ^{o,d}	IE ^e
BT	130.73	2.90	65.7	8.17
DBT	163.71	4.05	93.2	8.44
DMDBT	184.74	4.67	-	-
NAPH	135.39	2.84	72.3	8.144
FLUO	160.29	3.26	84.5	7.91

^a BT = benzothiophene; DBT= dibenzothiophene; DMDBT= 4,6-dimethyldibenzothiophene; NAPH= naphthalene; and FLUO= fluorene. ^b Values for accessible surface area (Å²) were obtained from DFT calculations at B3LYP/6-31G* level using Spartan'10 Software. ^c Log P values from Crippen Method as reported in NIST Webbook. ^d Standard sublimation enthalpy (kJ mol⁻¹, 298.15 K) as reported in NIST Webbook. ^e Ionization energies (IE, eV) as reported in NIST Webbook.

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