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Dimethyl sulfoxide as a green solvent for successful precipitative polyheterocyclization based on nucleophilic aromatic substitution, resulting in high molecular weight PIM-1

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Experimental Section

5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (TTSBI, 97%) was obtained from TCI (Europe), 2,3,5,6,-tetrafluoro-terephthalonitrile (TFTPN, 99%) P&M (Moscow, Russia). Potassium carbonate (K_2CO_3, >99.5%) was dried overnight at 160 °C. Solvents were purchased from Sigma-Aldrich : dimethyl sulfoxide (DMSO, ≥99%), tetrahydrofuran (THF, ≥99.0%), methanol (≥99.0%), chloroform ($CHCl_3$, 99.0%), were used as received.

Synthesis of PIM-1 in DMSO. 5.106 g (15 mmol) of TTSBI, 3.003 g (15 mmol) of TFTPN, 6.2 g (45 mmol) of K_2CO_3, 40 mL DMSO and 5 mL toluene were charged into a flask under argon and room temperature. The mixture was vigorously stirred (approximately 15000 rpm) by using a IKA high-speed homogenizer for 3 min at room temperature, then, placed in an silicon oil bath preheated to 60 (100, 120) °C for 2-7 h with low speed stirring (approximately 1000 rpm). Very thin yellow polymer powder was isolated by centrifugation and subsequent filtration. The rest of inorganic salts and DMSO were eliminated by washing with hot water and subsequent extraction in Soxhlet's apparatus by MeOH. ^{1}H and ^{13}C NMR spectra of studied compounds were recorded on a Bruker Avance^{TM} 600 spectrometer. Chemical shifts δ were determined using residual proton signals of the deuterated solvent as an internal reference. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.84 (s, 2H), 6.46 (s, 2H), 2.36 (d, J = 14.0 Hz, 2H), 2.19 (d, J = 13.5 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.70, 146.93 , 139.48, 139.20, 112.33, 110.56, 109.41, 94.12, 77.23, 77.02, 76.81, 58.82, 57.15, 43.62, 31.38, 29.94.

Thermogravimetric (TGA) studies of polymers were carried out on an MOM Q1000 derivatograph (Hungary) in air at heating rate of 5 K min^{-1} with a sample weight of ~20 mg. The IR absorption

spectra of samples were recorded as thin films or as KBr pellets on a Nicolet Magna_IR 750 FTIR spectrophotometer in the range of 4000–400 cm^{-1}. The reduced viscosity of the polymers was measured with an Ubbelohde viscometer at 25°C in 0.5 g dL^{-1} 1,1,2,2-tetrachloroethane solution. Apparent molecular weights and MWD were determined by size exclusion chromatography in chloroform as an eluent at1 mL min^{-1} and 25ºC on Agilent 1100 setup equipped with a UV-VIS detector and two Ultrastyragel Linear columns. Clarity GPC software was used for calibration according to PS standards and data processing. The samples for the analysis were prepared as 1 mg mL^{-1} solutions (dissolved overnight) filtered through pore 40 glass filters.

Table S1 Synthesis conditions and properties of samples.

Entry	Synthesis conditions				Yield[a)]	η_{red}[b)]	M_w	M_p	$\underline{PDI_{total}}$
	Solvent	T [^oC]	$wt_{monomer}/wt_{total}$ [%]	τ [h]	[%]	[dL g^{-1}]	[kDa]	[kDa]	*($PDI_{main\ peak}$)*
1	DMSO	60	14.1	7	95/3	0.46	52.1	36.4	4.3 *(2.4)*
2	DMSO	100	15.6	7	93/6	0.42	37.2	31.1	4.6 *(2.2)*
2a (sol)	DMSO	100	15.6	7	6 (sol)	-	29.3	25.4	4.8
3	DMSO	120	14.1	2	99/1	0.60	115	87.2	5.3 *(2.9)*
4	DMF[1]	65	7.5	72	83[c)]	0.54[c)]	85.0	80.2	5.7

[a)]main product (PIM-1 powder) / precipitate from the sol in DMSO; [b)]0.5 g dL^{-1} solution in 1,1,2,2-tetrachloroethane at 25 ^oC; [c)]after two reprecipitations from $CHCl_3$ into MeOH + extraction by hot DMA.

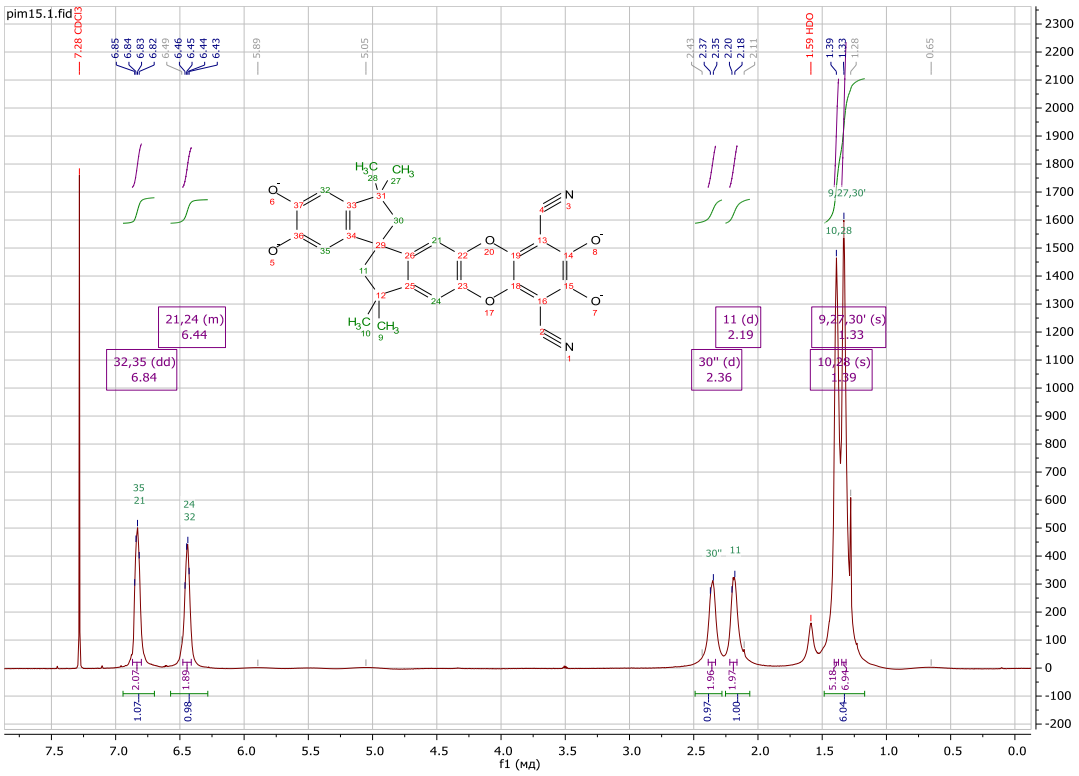

Figure S1 PIM-1 ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.84 (s, 2H), 6.46 (s, 2H), 2.36 (d, *J* = 14.0 Hz, 2H), 2.19 (d, *J* = 13.5 Hz, 6H).

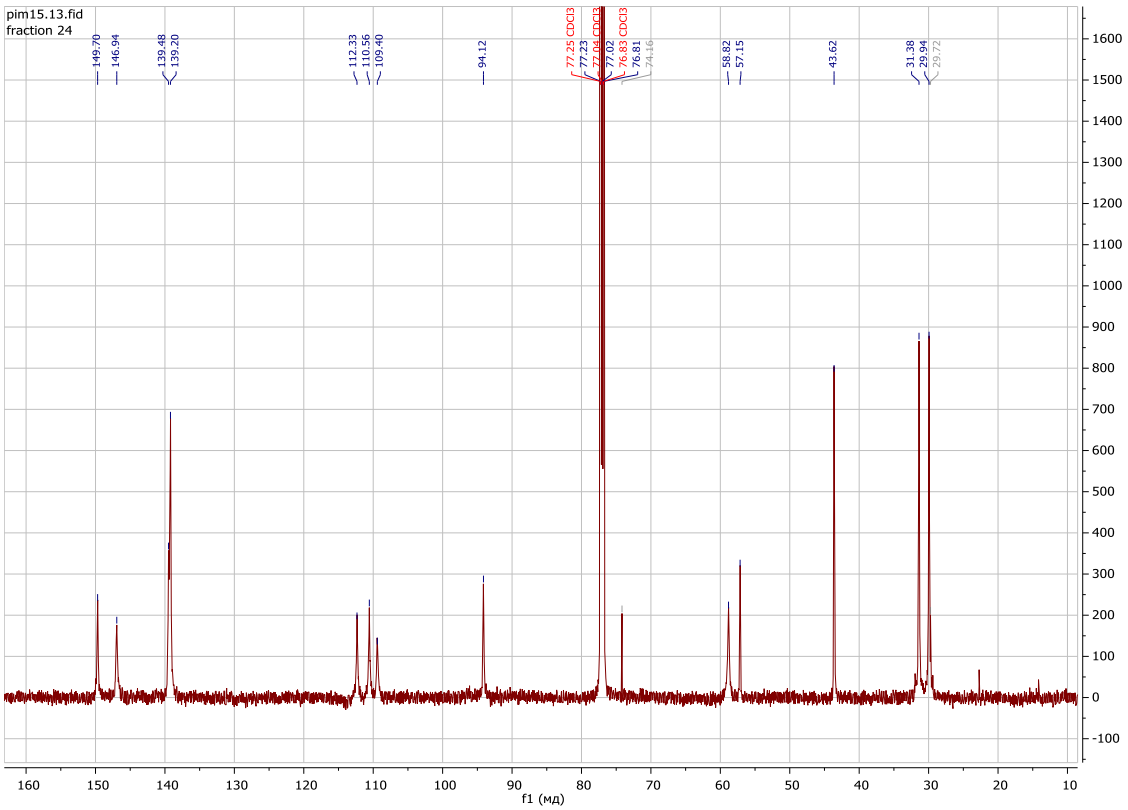

Figure S2 PIM-1 ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.70, 146.93, 139.48, 139.20, 112.33, 110.56, 109.41, 94.12, 77.23, 77.02, 76.81, 58.82, 57.15, 43.62, 31.38, 29.94.

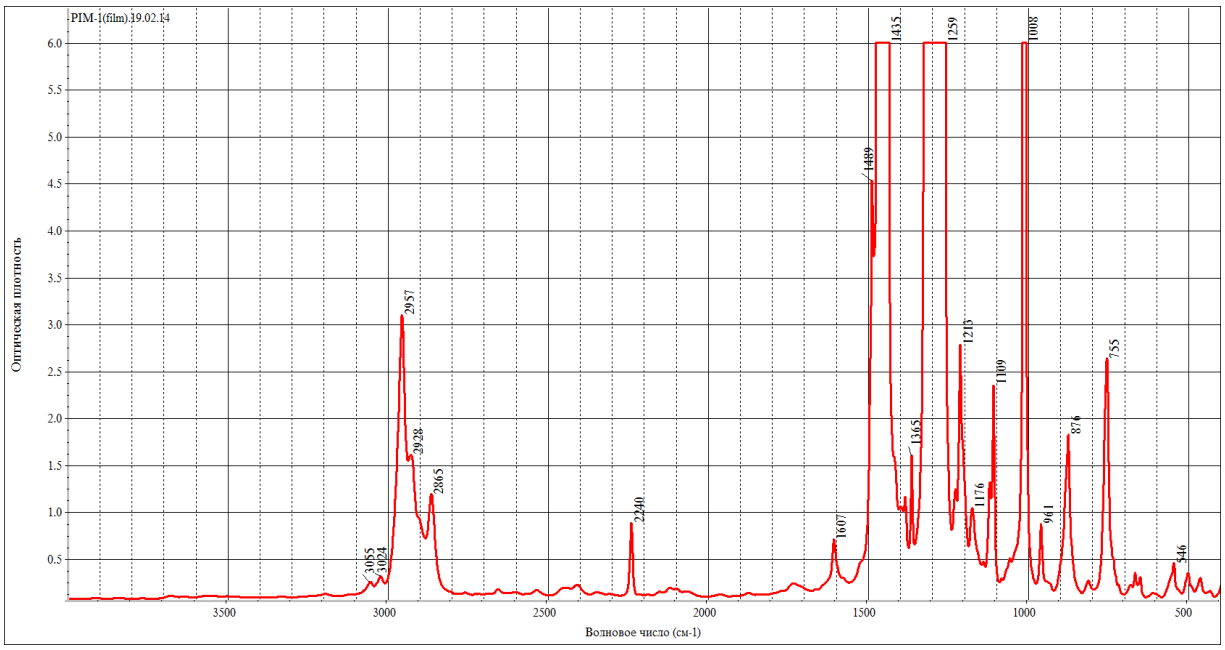

Figure S3 FT-IR of PIM-1.