Electronic supplementary materials *Mendeleev Commun.*, 2019, **29**, 663–665

New approach to chemical modification of PIM-1 for gas separation membranes

Igor I. Ponomarev, Konstantin A. Lyssenko, Dmitry Yu. Razorenov, Yulia A. Volkova, Ivan I. Ponomarev, Kirill M. Skupov, Zinaida S. Klemenkova, Ludmila E. Starannikova, Alexander Yu. Alentiev and Yuri P. Yampolskii

Pentafluorobenzoyl chloride and tetrafluoroterephthalonitrile were obtained from P&M (Moscow, Russia). 5,5',6,6'-Tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobiindane (TCI) was dried in vacuum at 140 °C. Potassium carbonate (K_2CO_3, >99.5%, Sigma-Aldrich) was dried before use overnight at 160 °C. Catechol, 2,4-dimethylaniline, benzanilide (**2a**), PCl_5 and $AlCl_3$, (Sigma-Aldrich) were used as received. Solvents were purchased from Sigma-Aldrich: *N,N*-dimethylacetamide (DMA, ≥99.0%), nitrobenzene, dimethyl sulfoxide (DMSO, ≥99%), methanol (≥99.0%), chloroform ($CHCl_3$, 99.0%), were used as received. PIM-1 was synthesized as reported [I. I. Ponomarev, I.V. Blagodatskikh, A.V. Muranov, Yu.A. Volkova, D.Yu. Razorenov, Iv.I. Ponomarev, K.M. Skupov, *Mendeleev Commun.*, 2016, **26**, 362], Mw=75 kDa (GPC in $CHCl_3$).

NMR ^1H and ^{19}F spectra were recorded on a Bruker Avance^{TM} 400 MHz spectrometer. Chemical shifts δ were determined using residual proton signals of the deuterated solvent as an internal reference.

The IR absorption spectra of samples were recorded as KBr pellets on a Nicolet Magna_IR 750 FTIR spectrophotometer in the range of 4000–400 cm^{-1}.

Mass-spectra of samples were recorded on MS Polaris Q,Thermo Electron Co., at 70 eV.

The melting points were determined on a Boetius hot-stage apparatus and are uncorrected.

The course of the reactions was monitored, and the purities of the reaction products were checked by TLC on Silufol UV-254 plates.

Crystals of **3b**·4$CHCl_3$ [$C_{54}H_{28}Cl_{12}F_{10}N_4O_4$, FW= 1412.20, cryst. $HCCl_3$ are triclinic, space group P-1, at 120(2) K a = 11.326(2) Å, b = 12.150(2), c = 12.738(3) Å, α = 68.59(3), β = =68.52(3), γ = 72.05(3)°, V=1487.4(7)Å^3, Z(Z') = 1(0.5), d_{calc}=1.577 g cm^{-3}, μ($Mo_{K\alpha}$)=6.39 cm^{-1}. Intensities of 14440 reflections were measured with Bruker APEX-II CCD [λ($Mo_{K\alpha}$) = =0.71072 Å, 2θ < 56°] and 7110 independent reflections (R_{int} = 0.0351) were used in the further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The refinement converged to wR_2= 0.1645 and GOF=1.018 for all independent reflections [R_1= 0.0582 was calculated against F for 4888 observed reflections with I>2σ(I)]. All calculations were performed using SHELXTL-2014/6.

Figure S1. NMR ^{1}H spectrum of **3a**.

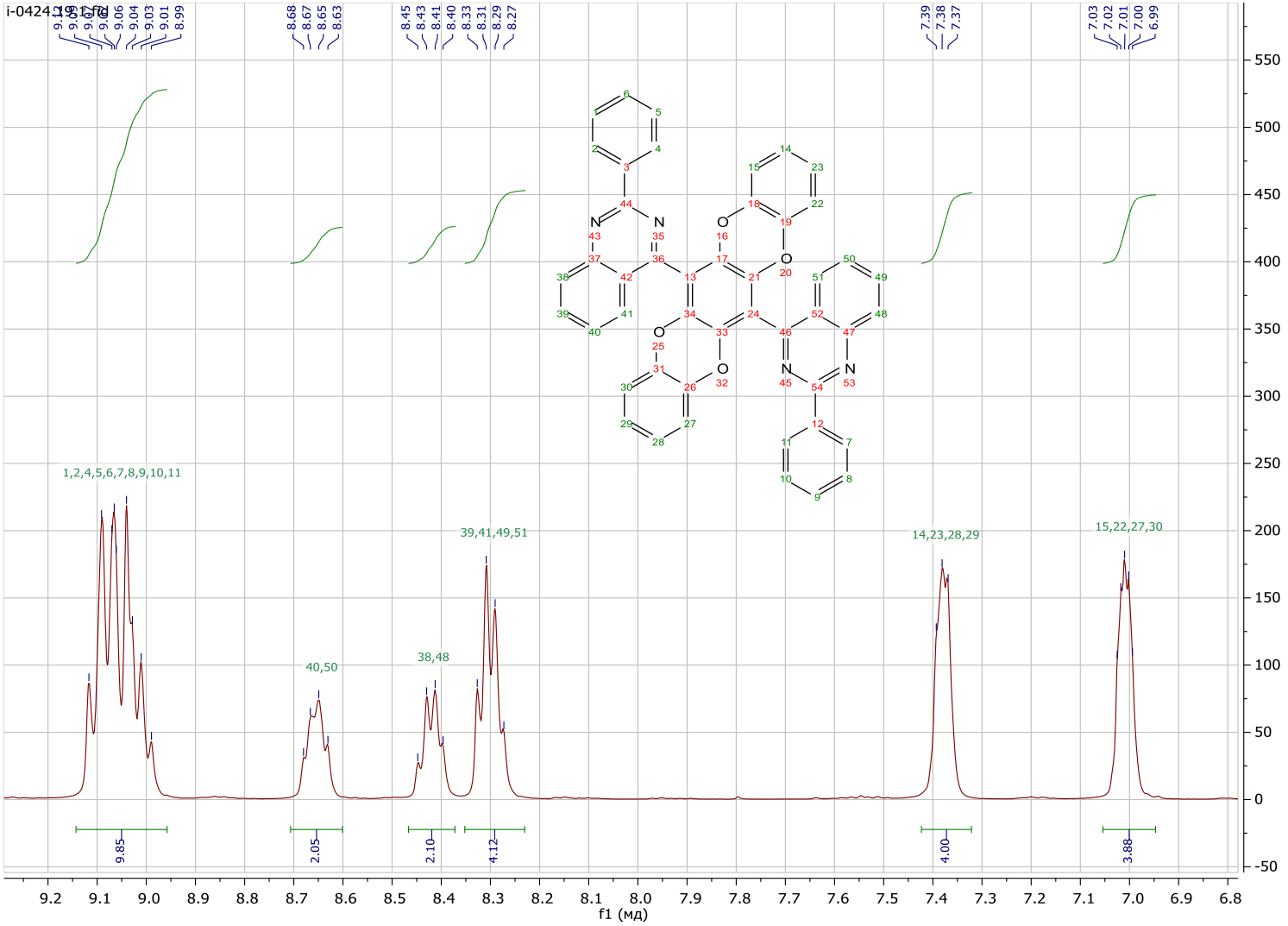

Figure S2. NMR ^{1}H spectrum of **3b**.

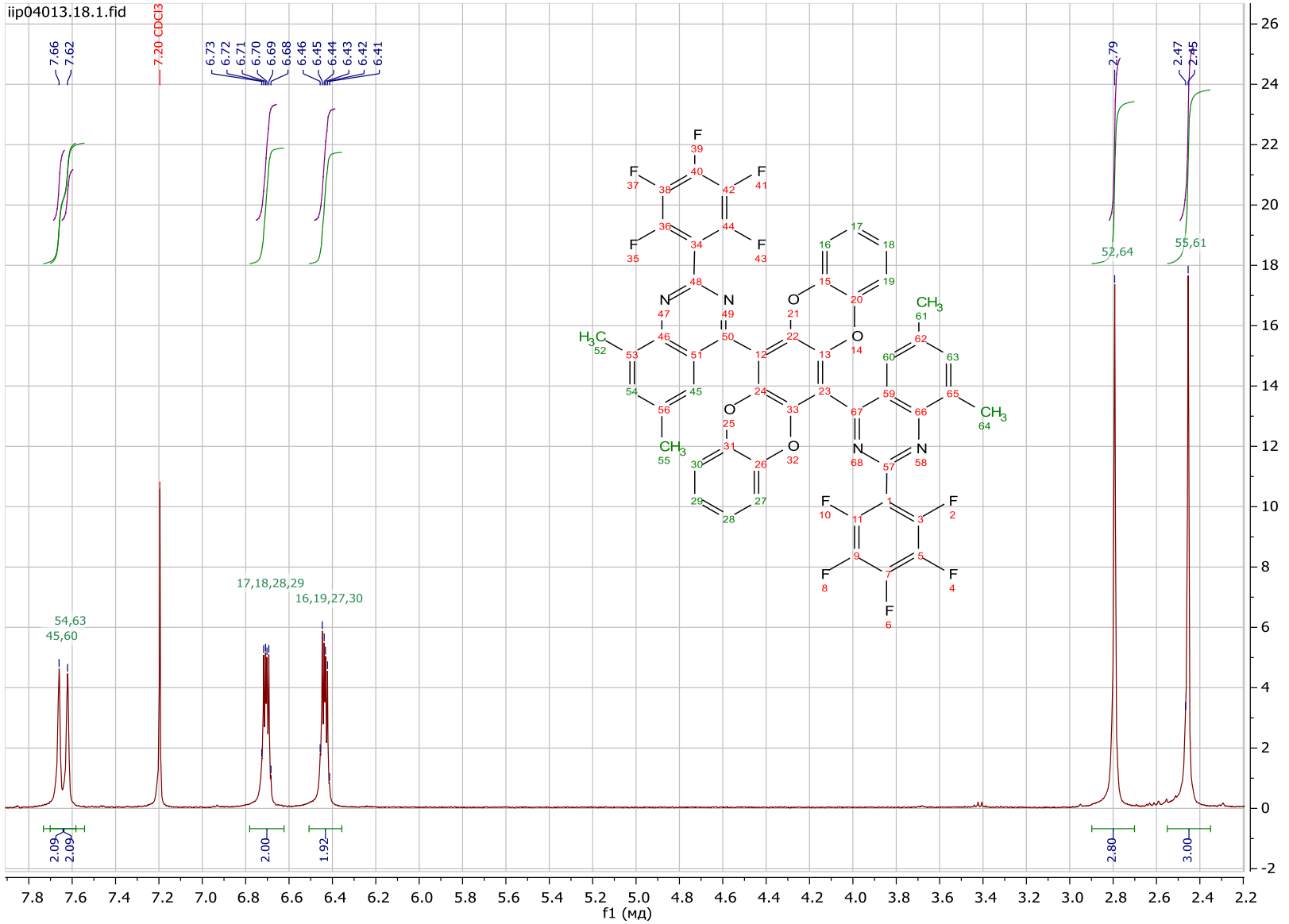

Figure S3. IR spectra of **1**, **3a** and **3b.**

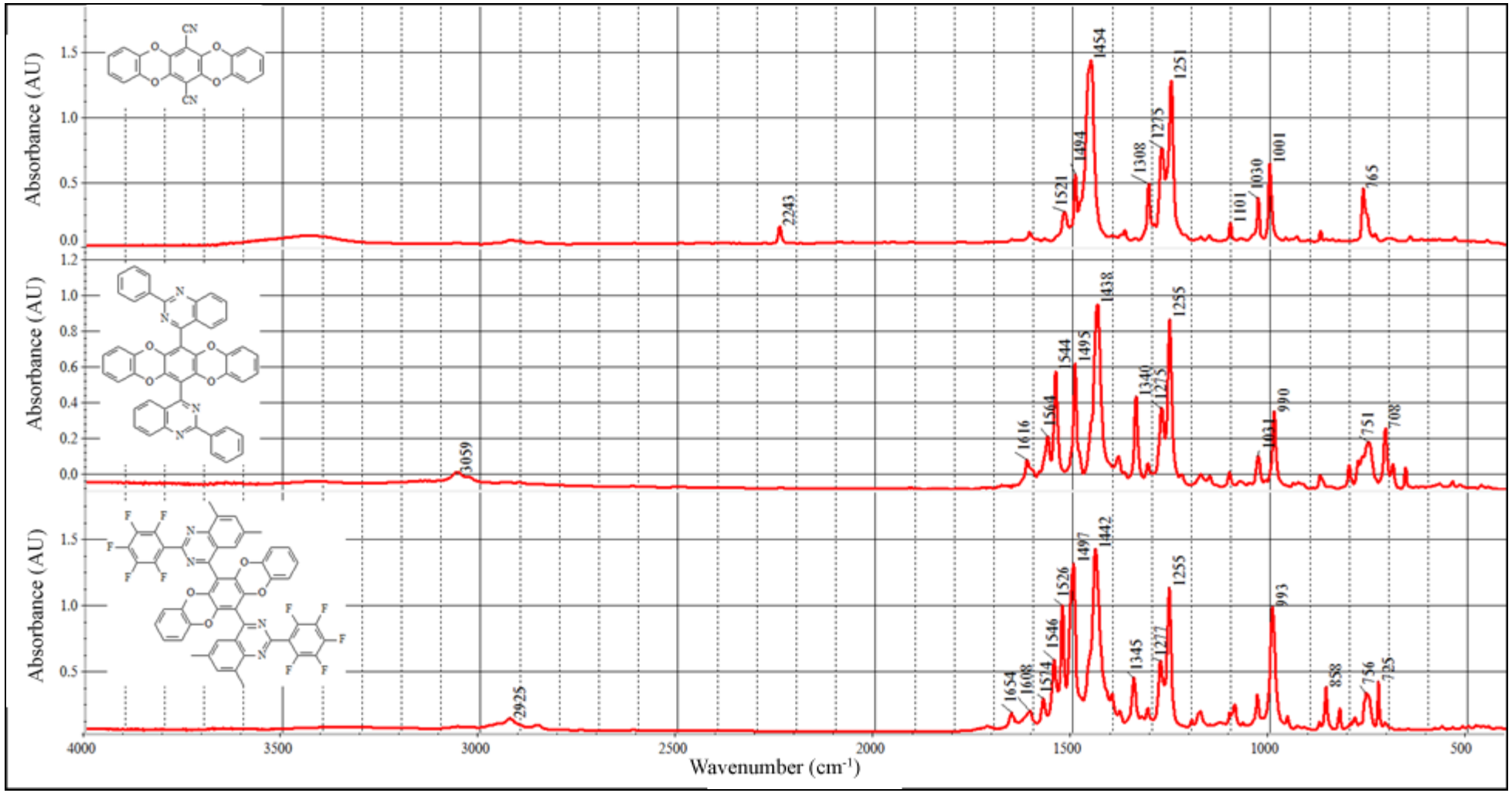

Figure S4. IR spectra of PIM-1 and PIM-1Q.