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Mendeleev Commun., 2019, **29**, 663–665
Mendeleev Communications

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

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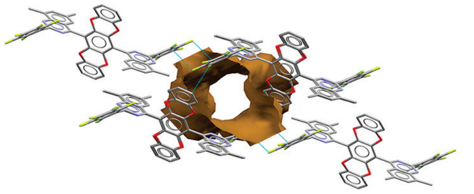
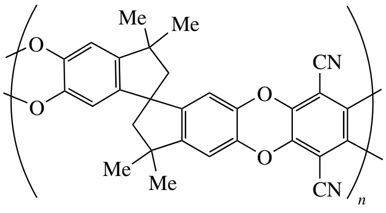
DOI: 10.1016/j.mencom.2019.11.020

Nitrile groups of model [1,4]benzodioxino[2,3-*b*]oxanthrene-6,13-dicarbonitrile were transformed into quinazoline moieties by heterocyclization with benzanilides. The procedure was extended for PIM-1 modification to obtain gas separation membranes with promising permeability and selectivity.



In recent years, PIM-1, a heterocyclic semi-ladder polymer with outstanding gas-separating properties, has become a topic of numerous reports.[1–3]

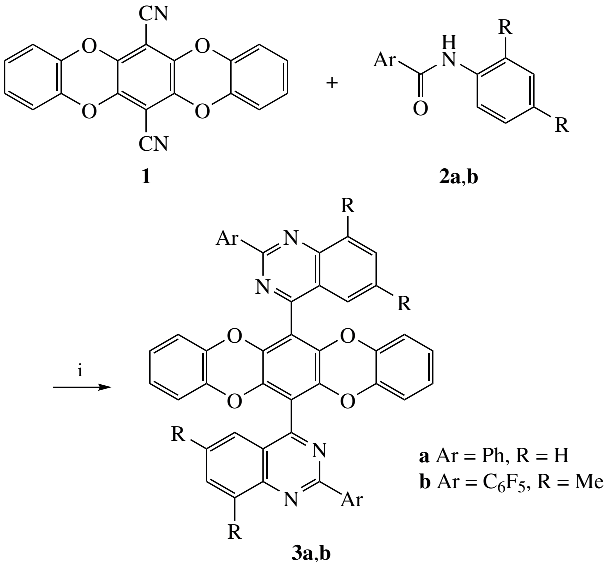


PIM-1

However, gas separation properties of membranes based on PIM-1 change in time due to polymer relaxation process. This physical aging is manifested in the changes of gas permeability and gas separation coefficients during long-term membrane tests thus preventing the production of industrial gas separation membranes based on PIM-1. The instability of the gas separation characteristics is connected with producing films from various solvents. Traces of moisture also affect the aging time, which significantly limits the PIM-1 applications. Even in such a rigid-chain polymer with glass transition temperature higher than its thermal decomposition point (450 °C), the rearranging of the nanostructure is observed even at room temperature. This was rationalized through secondary transition processes associated with the presence of residual solvents and moisture in the polymer, as well as with the possibility of small cooperative vibrational-rotational movements around a spatially hindered spiroindane groups.[1,2,4]

It is obvious that the chemical modification of PIM-1 and the changes in its spatial geometry should influence the gas separation and transport characteristics of materials based on it. For chemical modification of PIM-1 to access its analogues, some different reactions of its nitrile groups have been employed.[1,2,5–8]

In this work, model [1,4]benzodioxino[2,3-*b*]oxanthrene-6,13-dicarbonitrile **1** was involved in a heterocyclization with benzanilides **2a**,**b** in the presence of PCl_5 and $AlCl_3$ to construct quinazoline moieties (Scheme 1).† This heterocyclization provided nearly 100% yield of 2,4-diarylquinazolines and previously was successfully used in the synthesis of monomers for rigid-chain polyheteroarylenes.[9,10] Initial compounds **1**, **2a**,**b** were synthesized by known methods as described in Online Supplementary Materials.



Scheme 1 *Reagents and conditions*: i, $AlCl_3$, PCl_3, $PhNO_2$, 140 °C, 4 h.

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† *4,4′-[1,4]Benzodioxino[2,3-*b*]oxanthrene-6,13-diylbis(2-phenylquinazoline)* **3a**. A mixture of [1,4]benzodioxino[2,3-*b*]oxanthrene-6,13-dicarbonitrile **1** (0.34 g, 1 mmol), benzanilide **2a** (0.40 g, 2.03 mmol), PCl_5 (0.42 g, 2.03 mmol) and $AlCl_3$ (0.27 g, 2.03 mmol) in nitrobenzene (3 ml) was heated at 140 °C with stirring for 4 h. Nitrobenzene was evaporated under reduced pressure, and the brown solid residue was boiled in the mixture of H_2O (10 ml), MeOH (10 ml) and HCl (37%, 5 ml). The precipitate was filtered and dried in a vacuum oven. Yield 0.68 g (~97%). MS, *m/z*: $[M]^+$ 699, mp > 400 °C (decomp.). ^1H NMR

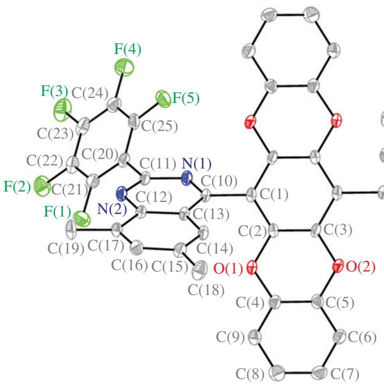


Figure 1 The general view of **3b** in representations of atoms by thermal ellipsoids (p = 50%).

Crystals of **3b** were obtained by crystallization from $CHCl_3$ and according to XRD it crystallizes as solvate with four $CHCl_3$ molecules.[‡] In a crystal (Figure 1), the molecule of **3b** occupies the centre of symmetry and is expectedly non-planar with nearly orthogonal arrangement of all cyclic fragments. The central fragment is slightly non-planar with the bent of the dibenzodioxine group by 17° in opposite directions in respect to central aromatic ring. The quinazoline ring is orthogonal to it with the torsion angle C(2)C(1)C(10)N(1) equal to 115.2°. Finally, the torsion angle N(2)C(11)C(20)C(25) is 49.7°. The molecule is surrounded by solvate molecules, therefore, the interatomic interaction between molecules **3b** is merely absent with the only exception of four shortened F···C (3.13 Å) contacts. The $CHCl_3$ molecules that are located within the channels form the numerous Cl···Cl interactions as well as rather strong C–H···O(1) and C–H···N(1) ones, with H···O distances being 2.4 and 2.2 Å, respectively. Such a type of arrangement of **3b** and solvate molecule leads to highly porous crystal packing with the volume of independent part of the channels equal to 481.48 Å^3 that is 32.4% of the total volume (Figure 2.) Thus, one can propose that compound **3b** can be of interest for the preparation of porous materials.

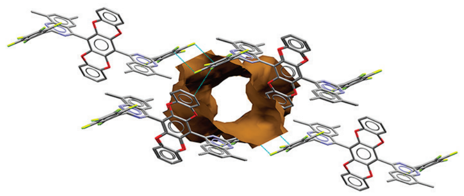
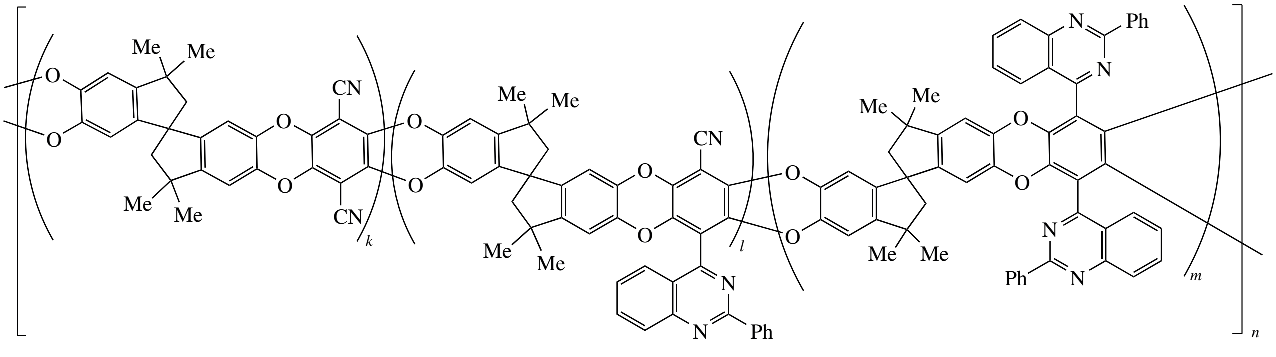


Figure 2 The porous crystal packing of molecules of compound **3b**. The solvate molecules are ommitted for estimation of pore volume.

The model experiments confirmed the possibility of using benzanilides **2a**,**b** for chemical modification of PIM-1.[§] The obtained sample PIM-1Q is soluble in chloroform, dichloromethane, THF and other solvents and can form homogeneous rather brittle films. The extent of modification in PIM-1Q was evaluated as 40% by ^1H NMR.

Permeability of the PIM-1Q film for various gases was found as follows (bar): He, 650; H_2, 1510; O_2, 550; N_2, 180; CO_2, 4130; CH_4, 335. Selectivity of the polymer film for various gases was found as follows: O_2/N_2, 3.1; CO_2/CH_4, 12; CO_2/N_2, 23; CO_2/O_2, 7.6; He/N_2, 3.6; He/CH_4, 1.9; H_2/N_2, 8.3; H_2/CH_4, 4.5. Further studies on PIM-1Q properties are planned in the nearest future.

This work was supported by the Russian Foundation for Basic Research (grant no. 18-08-00472 A). The X-ray studies were supported by the Ministry of Science and Higher Education of the Russian Federation and were performed using the equipment of Center for molecular composition studies of A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.



PIM-1Q

(400 MHz, CF_3COOD) δ: 9.14–8.96 (m, 10H), 8.71–8.61 (m, 2H), 8.47–8.37 (m, 2H), 8.35–8.25 (m, 4H), 7.42–7.34 (m, 4H), 7.05–6.97 (m, 4H).

4,4′-[1,4]Benzodioxino[2,3-*b*]oxanthrene-6,13-diylbis[6,8-dimethyl-2-(pentafluorophenyl)quinazoline] **3b** was obtained similarly from *N*-(2,4-dimethylphenyl)-2,3,4,5,6-pentafluorobenzamide **2b** (0.64 g, 2.03 mmol). Yield 0.92 g (~98%). MS, *m/z*: [M]$^+$ 935, mp 373–375 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.66 (s, 2H), 7.62 (s, 2H), 6.71 (dq, 4H, *J* 7.5, 3.8 Hz), 6.43 (dq, 4H, *J* 7.5, 3.8 Hz), 2.79 (s, 6H), 2.45 (s, 6H).

[‡] *Crystal data for* **3b**·4$CHCl_3$. $C_{54}H_{28}Cl_{12}F_{10}N_4O_4$, M = 1412.20, triclinic, space group $P\bar{1}$, at 120(2) K a = 11.326(2), b = 12.150(2) and 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}, $\mu(\text{Mo}_{K\alpha})$ = = 6.39 cm^{-1}. Intensities of 14440 reflections were measured with Bruker APEX-II CCD [$\lambda(\text{Mo}_{K\alpha})$ = 0.71072 Å, $2\theta < 56°$] 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 $I > 2\sigma(I)$]. All calculations were performed using SHELXTL-2014/6.

CCDC 1895905 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

[§] A solution of PIM-1 (0.46 g, 1 mmol) in nitrobenzene (6 ml) was mixed with **2a** (0.40 g, 2.03 mmol), PCl_5 (0.42 g, 2.03 mmol), $AlCl_3$ (0.27 g, 2.03 mmol) and heated at 140 °C with stirring for 6 h. Nitrobenzene was evaporated under reduced pressure, and the brown residue was boiled with the mixture of H_2O (10 ml), MeOH (10 ml) and HCl (37% aq., 5 ml). The precipitate was filtered, dried in a vacuum oven and re-precipitated from $CHCl_3$ with EtOH. PIM-1Q films for the gas separation test were prepared from $CHCl_3$ solution on glass plates.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.11.020.

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Received: 29th April 2019; Com. 19/5903