Dye-based covalent organic networks

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Abstract

This contribution presents four dye-based CONs derived from the reaction of triformylphloroglucinol with thionin acetate (RIO-43), safranin chloride (RIO-51), phenosafranin (RIO-47), and Bismarck brown Y (RIO-55). These materials, called Covalent Organic Networks (CONs), are insoluble solids formed by organic lamellar stacked structures and present permanent porosity, light absorption across the whole visible spectrum, fluorescence, ion exchange capability, and ion and electron conductivity. Periodic DFT calculations carried out indicated that the bent nature of most of those building blocks affords conductive extended materials containing pores with the shape of three-petal flowers, with the anion positioned at the petals. The turbostratic disorder makes only the center of the flower-shaped pores accessible, decreasing the specific surface areas. The material that has a higher surface area is the one derived from thionin acetate (RIO-43), such as the highest electrical conductivity (1.96 × 10⁻⁷ S cm⁻¹), followed by RIO-47 (1.12 × 10⁻⁷ S cm⁻¹), RIO-55 (1.58 × 10⁻⁷ S cm⁻¹) and RIO-51 (3.26 × 10⁻⁷ S cm⁻¹).

1. Introduction

Dyes have been used for thousands of years throughout the history of mankind. Employed as pigments for clothing, paintings, writing, cosmetics, and several different applications the use of dyes holds a special connection with the development of human civilizations. Most available dyes came exclusively from natural sources until the middle of the 19th century when a great chemical effort was directed towards the production of new synthetic organic dyes that have different colors and could be produced on large scale [1]. This effort combined with the development of new industrial production methods contributed to a genuine color revolution, which democratized access to colorized objects and clothing [2].

Within the different classes of dyes, organic dyes are especially interesting due to their unique physical, chemical, and biological properties. Particularly the optical absorption characteristics, structural diversity, low cost, and large-scale availability make organic dyes a fascinating choice for technological applications. Several applications of organic dyes have already been reported such as solar cell sensitizers [3–5], fluorescent labels [6], organic electronics [7], photoredox catalysts [8–10], among many others. However, the use of these materials as building blocks for assembling reticulated heterogeneous materials is still unexplored.

Covalent Organic Networks (CONs) are a class of 2D porous reticulated materials built-up by organic building blocks presenting different topologies in a predictable manner that is comparable to a molecular equivalent of interlocking toy bricks [11]. Their topologically well-defined chemical structures make these porous materials promising candidates for use in a myriad of important applications such as gas adsorption [12], proton conduction [13], optoelectronics [14], energy storage [15], catalysis [16], among others [17]. However, despite the many potential interesting applications of these materials, one of the main drawbacks...
of their large-scale production is their cost. Thus, employing inexpensive building-blocks, such as commercial dyes, could be an interesting alternative for obtaining cost-effective CONs.

In the present study, we present four dye-based Covalent Organic Networks (CONs) named RIO-43, RIO-47, RIO-51, and RIO-55. Those materials were assembled by an imine condensation reaction of triformylphloroglucinol with commercially available ditopic azo and ionic dyes (figure 1): thionine acetate (Lauth’s violet) (affording RIO-43), safranin (affording RIO-51), phenosafranin (affording RIO-47), and Bismarck brown Y (affording RIO-55). The resulting materials presented a lamellar structure with permanent porosity and high surface areas, ranging from 220 to 360 m² g⁻¹. They all presented a wide light-absorbing profile within the visible range due to their large π-conjugated system and presented conductivities in the range of 10⁻⁷ to 10⁻³ S cm⁻¹. Ionic absorption tests also revealed that RIO-55 has a high uptake capacity and high selectivity for SO₄²⁻ adsorption, indicating that dye-based CONs can be an excellent alternative for the production of functional and low-cost porous 2D materials.

2. Results and discussion

The layered (2D) porous materials called RIO-n (our acronym for Reticular Innovative Organic frameworks) were obtained by imine condensation of a triangular and tritopic building block (triformylphloroglucinol, TFPG) with ditopic organic dyes: thionin acetate (RIO-43), safranin (RIO-51), phenosafranin (RIO-47), and Bismarck brown Y (RIO-55) in a sealed high-pressure vessel under solvothermal conditions. Optimization of the reaction conditions showed that the traditional solvothermal method (1,4-dioxane, 6 M acetic acid, 120 °C, 72 h under stirring) afforded materials with improved specific area and crystallinity. We also noticed that TFPG in molar excess resulted in an improvement in the specific area for all resulting RIOs (see Supporting Information section for details).

Fourier transform infrared spectroscopy (FTIR) and solid-state ¹³C NMR spectra (CP-MAS) confirmed the proposed chemical structures (figures S2 and S3). Attribution of the bands was made based on analysis of the vibrational bands of the model compounds obtained from DFT calculations at B3LYP/6-31 G(d,p) level on the optimized structures of a model compound (for details see SI). FTIR measurements of all RIOs present the appearance of a ν(C=O enol) stretching band at ~1590 cm⁻¹, corresponding to the aldehyde
carbonyl group, and a $\nu(N-H)$ stretching at $\sim3400 \text{ cm}^{-1}$, resulting from the imine condensation reaction between -NH$_2$ and -CHO groups. RIO-43, RIO-47, and RIO-51 present a $\nu(C=\text{N})$ stretching at $\sim1484 \text{ cm}^{-1}$, $1567 \text{ cm}^{-1}$, and $1527 \text{ cm}^{-1}$, respectively, corresponding to the dye-residue moiety. RIO-55 also presents the $\nu(C-N=\text{N})$ stretching at $\sim1440 \text{ cm}^{-1}$, showing that the dye-residue core structure remained unchanged. The $^{13}$C CP-MAS solid-state NMR presented signals corresponding to C=O at $\sim185 \text{ ppm}$ and C=C at $\sim107 \text{ ppm}$ for all structures, which shows the presence of keto-enol tautomerism [18] in all synthesized RIOs. FTIR of azo-dye-based RIO-55 also showed a characteristic $\nu(\text{Ar-N})$ stretching at $1280 \text{ cm}^{-1}$ and $\nu(N-H)$ at $3420 \text{ cm}^{-1}$ due to the free -NH$_2$ groups inside the pore.

The experimental Powder x-ray Diffraction (PXRD) patterns (figures 2(i)–(l)) reveal a major broad peak at $2\theta = \sim28^\circ$ for all RIOs, consistent with an interplanar distance of $\sim3.2 \text{ Å}$, referring to the $\pi - \pi$ stacking between the 2D layers. RIO-43 and RIO-51 also presented a broad peak at $2\theta = \sim11^\circ$, due to an interplanar distance of 7.5 Å. The crystallinity profile presented a slight improvement after the supercritical CO$_2$ (scCO$_2$) activation of the samples.

Textural analysis from isothermal gas (N$_2$) sorption measurements (figures 2(a)–(d)) revealed that all RIOs present permanent porosity and a combination of type-I and type-II isotherms, according to the classification of IUPAC (International Union of Pure and Applied Chemistry) [19], which is a common feature presented by several lamellar materials [21]. In fact, all isotherms present an intermediate character between H3 and H4 type hysteresis loop, which is an indication of wide to narrow slit type pores. These findings are consistent with the results of the PDRX, which showed a stacked lamellar material with a low degree of ordering degree between the layers.
The specific surface areas calculated from the gas adsorption isotherms by the Brunauer–Emmett–Teller (BET) method \[22\] were 361 m$^2$ g$^{-1}$ (RIO-43), 220 m$^2$ g$^{-1}$ (RIO-51), 320 m$^2$ g$^{-1}$ (RIO-47) and 280 m$^2$ g$^{-1}$ (RIO-55). Supporting Information section presents the comparative areas before and after supercritical CO$_2$ (scCO$_2$) activation. The values of the specific surface area presented by all RIOs are not as high as other high crystalline 2D porous covalent materials, such as COFs. Nevertheless, the presented data are in the same order of magnitude of other porous lamellar materials \[20, 23\]. The pore size distribution, figures 3 ((a)–(d) inserts), shows the presence of micropores of 13, 15 and 13 Å for RIO-43, RIO-51, and RIO-47, respectively, and mesopores of 34 Å for RIO-55. Moreover, all materials present a constant incidence of larger pores with a size up to 50 nm.

Multiple structural factors are associated with the low specific area, low crystallinity, and the pore size distribution profile presented by RIOs. The presence of ions and solvated species into the pores, for example, provide severe limitations on pore accessibility and relative stacking of the layers for RIO-43, RIO-51, and RIO-47. Additionally, the non-linearity of the building blocks and their low symmetry can promote the emergence of defects in the structure, i.e. stacking faults, amorphous areas, and the development of a turbostratic disorder, thus decreasing the crystallinity and generating the formation of a myriad of meso and macropores. Consideration of the low nucleophilicity of the charged building blocks and the repulsion between charged sheets in CONs may also inhibit the regular stacking in such structures. For RIO-47 and RIO-51 there is still a phenyl group linked to the cationic site pointing towards the pore structure that provides large steric interactions and hinders the accommodation of the ions in the structure.

Based on these results, it is possible to visualize these materials as lamellar with well-defined chemical structure, forming pores with sizes compatible with that expected due to their topology, stacked in such a disordered manner that forms a broad distribution of slit type pores and generates a low crystallinity profile.
This disordered behavior is presented by many 2D covalent polymers, where the growth kinetics and geometric features of the structure prevent the formation of the expected thermodynamically stable crystalline form and deviates the structure to a low ordered phase [24].

Thermogravimetric analysis (TGA) showed three main regions: an initial weight loss in the range of 10%–20% up to 100 °C, due to solvent loss; a region of stability of the weight loss from 100 °C to approximately 300 °C for RIO-43, RIO-47, and RIO-51 and to a higher temperature (450 °C) in the case of RIO-55; and from this temperature to 600 °C, where the CON is decomposing (see figure S8). RIO-43 exhibits an initial weight loss of 20%, which corresponds to approximately 5 EtOH per acetate per pore. RIO-47 and RIO-51 present about 10% of initial weight loss corresponding to about 2 EtOH molecules per chloride ions within the pores. RIO-55, on the other hand, showed an initial weight loss of 17%, corresponding to approximately 1 EtOH molecule per chloride within the pore. RIO-43, RIO-47, and RIO-51 were thermally stable up to ~300 °C, and up to 450 °C in the case of RIO-55.

DFT calculations under periodic boundary conditions, using PBE-D3 functional for the idealized structures of RIO’s, were carried out to improve the understanding of their structural characteristics. The optimized geometries showed that for RIO-47, RIO-43 and RIO-51 the equilibrium structure forms a buckled-AA stacking, as shown in figure 3. For all structures, the interlamellar distance ranged from 3.5 to 3.6 Å, compatible with the interplanar distance found in the experimental PDRX profile, figures 2(i)-(l). The calculations show that for RIO-47 and RIO-51 the phenyl displays a key role in inducing the structure to assume a buckled conformation. The calculations also show that all RIO’s presented a metallic electronic behavior.

Figures 2(e)-(h), showed that RIOs a wide absorption range in the UV–Vis spectra and also presented fluorescence (figure S8). The reticulated extended structure results in the formation of a large π-conjugated system along the molecular backbone, which a high electro-relocation and transitions of π → π∗ type. The fluorescence spectra of RIOs indicate a hypsochromic shift of the bands concerning their parent dyes (figure S7), which is a direct consequence of the reticular structure formation.

In order to access the ion adsorption capabilities of the new synthesized dye-based CONs, RIO-43 and RIO-55 were evaluated in terms of ion adsorption isotherms with sulfate (SO₄²⁻) and nitrate (NO₃⁻) and the results are presented in figure 5. The maximum adsorption capacity (Q_max) and adsorption equilibrium constant (K_L) were determined based on a Langmuir model fitting [25]. The SO₄¹⁻² uptake from aqueous solution (Q_max) was 8.41 mg g⁻¹ (K_L = 0.165) for RIO-43. RIO-55 presented high sulfate adsorption with 52.67 mg g⁻¹ (K_L = 1.70) for RIO-55. The values of Q_max presented by both CONs were low when compared to other anion exchange materials [26]. The NO₃⁻ uptake of RIO-43 was below the detection limit of the equipment and therefore could not be determined. This result shows that its micropores are too small to even allow ion exchange. Interestingly, however, RIO-55 presented nitrate adsorption with Q_max = 15.05 mg g⁻¹ and K_L = 0.244. The results for RIO-55 are extremely encouraging, and this material can be an excellent ion adsorbent with high selectivity for SO₄⁻².

After the discovery of graphene, several conjugated materials have been synthesized because of their charge conducting properties, especially bidimensional networks. Tablets made of the pressed powders
Figure 5. Adsorption isotherms for sulfate in RIO-55 (a) and RIO-43 (b) and nitrate in RIO-43 (b) and its respective linearized plots (inserts).

(60KN) of RIOs were evaluated in terms of electrical conductivity employing the Four Probe method, exhibiting interesting values of electrical conductivity (details at the SI section). RIO-43 has the highest conductivity ($1.96 \times 10^{-5}$ S cm$^{-1}$), followed by RIO-47 ($1.12 \times 10^{-7}$ S cm$^{-1}$), RIO-55 ($1.58 \times 10^{-7}$ S cm$^{-1}$) and RIO-51 ($3.26 \times 10^{-7}$ S cm$^{-1}$). These values indicate that RIOs are semiconductors. Some reported COFs, MOFs, and iCONs have similar conductivity as shown in table 1.

As the theoretical calculations revealed that these RIOs should present a metallic electronic behavior, their low electrical conductivity values are mainly a consequence of structural defects or low crystallinity. Bein and co-workers found a correlation between the electrical conductivity and the crystallinity of the material [27]. In fact, RIO-43, with a slightly higher crystallinity than the others, also has a slightly higher value of electrical conductivity, while others tend to be less conductive due to their low crystallinity. Thus,
the increase of the crystallinity will possibly improve their conductivity, and this is a goal to be pursued in the future studies. RIO-43 was exposed to iodine vapor for 48 h in order to improve its conductivity value. In fact, its electrical conductivity increased to $10^{-3}$ S cm$^{-1}$ after doping. Similar value was found to TTF-COF thin film$^{[14]}$ after exposure to iodine. Doping of other RIOs will be implemented in future studies.

SEM analyses of the materials have shown their layered morphology, although with low crystallinity (figure 4). EDX mapping analysis (figure S13) of the images confirm their expected elemental analysis, being constituted solely of C, N, O, S (RIO-43) and C, N, O, Cl for RIO-47, RIO-51 and RIO-55.

3. Conclusions

Dye-based Covalent Organic Networks, named RIO-43, RIO-51, RIO-47, and RIO-55, were synthesized from low-cost building blocks, most that are commercially available. All RIOs presented permanent porosity and high BET surface areas. RIOs have shown to be promising materials as semiconductors and selective sulfate adsorbents. Besides, they have the potential for use as sensors, organic electronics, and heterogeneous photocatalysts due to their visible light absorption/emission properties. These and related materials also have a huge potential as adjustable as semiconductors or conductors due to their electrical conductivity, with the advantage of having chemical structural versatility. This would allow tailor-made porous materials, which present both ion and electrical conductivity in addition to their photochemical and photophysical activity

4. Methods

The synthesis of RIO-43 (from thionin acetate), RIO-51 (from safranin), RIO-47 (from phosphafranin) and RIO-55 (from Bismarck brown Y, 4,4′-(m-Phenylenedisazo)bis-m-phenylenediamine dihydrochloride) was carried out in a cylindrical 48 ml sealed high-pressure vessel (Chemglass, model CG-1880-04) under solvothermal conditions. The reactions were carried out in solvothermal conditions using 1,4-dioxane as a solvent and acetic acid (HOAc, 6 M) at 120 °C under stirring for 72 h. The resulting porous network formed by these materials is semi-filled by the ions present in the structure of the building blocks, occurring solvation of the molecules by the synthesis process and/or by air humidity. Therefore, several tests were performed in different synthetic conditions (solvant change, catalyst concentration, reaction time, post-synthesis washing and some reagents, among others, see Supporting Information for details). The resulting materials are dark and insoluble powders, leaving some traces of precursors, but which are removed by Soxhlet extraction. Supercritical drying using scCO2 was also used as the post-synthesis method to activate the pores. The Supporting Information section contains details of these procedures.

The textural characterization was made through the physical adsorption of N2 at 77 K. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method, in the adsorption branch, in the range of 0.05–0.20 P/P0 (relative pressure). The pore size distribution was calculated using the Nonlocal Density Functional theory (NLDFT) method, on carbon and slit/cylindrical pore model, as implemented in the software NovaWin version 10.01 of Quantachrome Nova 2200e. 13C CP-MAS solid-state NMR experiments were recorded on the AvanceIII-400 MHz spectrometer. RIOs were also characterized by UV–Vis diffuse reflectance spectroscopy, FTIR, TGA, and PXRD.

The ion adsorption analysis was made by ion chromatography using a Dionex ICS 5000 chromatograph. The sulfate, nitrate and phosphate anions used as adsorbates were analyzed by Dionex IonPac AS19. At first, SO4$^{2-}$ solutions of ~10 ppm to ~ 40 ppm with a range of 5 ppm were prepared. Aiming to observe ionic species selectivity, some RIOs were exposed to solutions containing SO4$^{2-}$, and NO3$^{-}$, under the same conditions. The amount of the RIOs in direct contact with the solution was 10 mg for 10 ml and the contact time was 40 min. Ion chromatography analysis of the solutions was carried out in triplicates. For each

Table 1. Electrical conductivity comparison of some porous ionic materials.

| Porous material   | $\sigma$ (S/cm) | Ref.        |
|------------------|----------------|-------------|
| RIO-43           | 1.96 ± 1.44 × 10$^{-5}$ | This work  |
| RIO-43 with I$_2$| 1.14 ± 0.47 × 10$^{-3}$ | This work  |
| RIO-47           | 1.58 ± 0.45 × 10$^{-7}$ | This work  |
| RIO-51           | 3.26 ± 0.47 × 10$^{-7}$ | This work  |
| RIO-55           | 1.12 ± 0.44 × 10$^{-7}$ | This work  |
| DPP2-HHTP-COF    | 2.2 × 10$^{-6}$, 2 × 10$^{-7}$ | Bein et al [27] |
| TTF-Ph-COF       | 10$^{-5}$       | Bein et al [28] |
| TTF-Py-COF       | 10$^{-6}$       | Bein et al [28] |
material, the uptake capacity (Q_{\text{max}}), and Langmuir adsorption equilibrium constant (K_L), were derived from the coefficients obtained by nonlinear regression of a Langmuir isotherm plot. Uptake capacity (mg/g or mmol/g) was calculated according to the following equation:

$$Q = \frac{(C_0 - C_e)V}{M \cdot m} \quad (1)$$

where $C_0$—initial element concentration in aqueous solution (mg/L); $C_e$—element concentration in aqueous solution after contact with adsorbent (mg/L); $V$—the volume of aqueous solution (L); $M$—atomic mass of the element; $m$—the mass of the adsorbent used (g). 

Supporting Information presents further details of the ionic adsorption procedures.

The measurements of electrical conductivity were made by Four Probe method \cite{29}, where current is applied between the external terminals, with the help of a Keithley model 6220 voltage source and the potential difference is the temperature between the internal terminals. The calculation of electrical conductivity ($\sigma$) follow according to equation (2):

$$\sigma = \frac{I \cdot \ln 2}{V \cdot \pi \cdot \frac{1}{w}} \quad (2)$$

where $I$ is current (Ampère, A), $V$ the electrical potential difference (volts, V), $w$ the thickness (cm) and $(\ln 2)/\pi$ is a correction factor. For this analysis, the samples were pressed into solid pellets. See table S2 for more details.

The diffuse reflectance spectra in the UV–Vis region were recorded by a Shimadzu UV 2600 spectrophotometer through absorbance mode, for solid-state materials, in the 200–800 nm range. The samples were diluted in BaSO$_4$.

The fluorescence spectra in the UV–Vis region were recorded on a time-resolved fluorimeter, coupled to an Edinburgh Instruments fluorescent Xenon lamp model FL900, obtained by exciting the samples at 450 nm (RIO-43), 450 nm (RIO-51), 350 nm (RIO-47) and 350 nm (RIO-55). The emission spectra (solid-state) covers a large region for all the samples. A quartz support front face was used for these analyses (see Supporting Information).

SEM images were obtained through a JEOL JSM-7100 F microscope equipped with EDS Oxford Micro X-MAX-80 and operated at 10 kV. The samples were placed on carbon tape.

Geometry optimization of the model structures was carried out using DFT calculations under periodic boundary conditions approach with Quantum Espresso code version 6.4.2 \cite{30,31}. Exchange and correlation effects are treated with generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional and nuclei and core electrons are described by ultrasoft pseudopotentials \cite{32}. The van der Waals interactions were treated with the D3 correction method of Grimme et al \cite{33}. The Kohn–Sham orbitals are expanded in a plane-wave basis set with a kinetic energy cutoff of 40 Ry and 380 Ry for charge density. The first Brillouin Zone integrations were performed with $2 \times 2 \times 4 \Gamma$-centered Monkhorst–Pack \cite{34} k-point sampling. Atomic positions and cell parameters were simultaneously fully optimized until the forces acting on the atoms were lower than 10$^{-3}$ Ry Bohr$^{-1}$.

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