

“Everything is surface”: tunable polymer organic frameworks with ultrahigh dye sorption capacity†

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Carbonaceous polymer networks with tunable porosity were found to behave as exceptional adsorbents toward large organic molecules such as organic dyes.

Sorption materials are of key importance for many chemical processes, and of particular interest for the purification of air and drinking water. Performance at rather low prices is a key issue in many of those applications, and in security sensitive applications absolute capacity is an unavoidable demand. In order to extend the performance of classical active carbon materials, more and more effort is now being made towards the development of scaffolds containing organic building blocks, which—due to their functional diversity—allow for exquisite control over the chemical nature of the surface areas and the sorption properties of the resulting frameworks. Purely organic, micro- and mesoporous materials are however still a contemporary field of materials chemistry.^{1–5} In addition: sorption performance is not only a question of absolute surface area and its chemical nature; accessibility throughout a designed pore channel system also has to be established. This is why carbons with the highest specific surface areas (as determined by gas sorption) are not necessarily the best performing systems, and other structural characteristics have to be looked for.⁶ In particular for larger sorbent molecules such as dyes, pure microporosity is not useful at all.

The ideal sorbent in such cases would be a structure where all parts of the porous structural network are in fact at the surface of a super-micropore or a mesopore, *i.e.* a structure where “everything is surface”. Such structures with extremely high surface areas and well defined porosity are indeed provided by metal–organic frameworks, and the gas sorption capacities are correspondingly high.^{7,8} For such regular systems, however, pore filling is strongly diffusion limited (as all sorbent molecules have to pass through the small pore openings already at the outer surface, as for example seen in zeolites) and thus the development of a hierarchical porous system containing both supermicropores and mesopores is highly beneficial.

Recently, we introduced a new dynamic polymerization system that allows the formation of porous crystalline or amorphous triazine-based frameworks through the reversible ionothermal trimerization of aromatic nitriles.⁹ Using this approach, highly porous organic materials with high thermal and chemical stability could be prepared conveniently and from simple monomers. Consecutive rearrangement reactions from those triazine-based microporous scaffolds were shown to lead to a self-organized structural evolution towards hierarchical micro- and mesoporous polymers with well defined pore sizes, exposing surface areas of up to 3200 m² g^{−1} at the same time.¹⁰

In this communication, we will quantify the sorption of different dyes onto those structures. It will be shown that the performance of appropriately designed polymer frameworks can clearly exceed that of standard active carbons, reaching values of up to 1.3 g adsorbed material per g sorbent at reasonable binding strength and dynamics.

For comparison, two different aromatic dinitriles were polymerized leading to three different scaffold structures, as described in our previous publications (the BP sample was prepared from 4,4'-dicyanobiphenyl, whereas DCB1 and DCB2 were prepared from 1,4-dicyanobenzene using different reaction conditions, see ESI†).^{10,11} The specific surface areas, absolute porosity and mesopore size of the samples are summarized in Table 1.

The systems cover specific surface areas of 1400–3270 m² g^{−1} and average mesopore sizes of 2.9–6.3 nm. Onto those systems, four rather different dye probes were adsorbed (Methyl Orange, Methylene Blue, Reactive Blue 2, Yellow 3G-P). These dye structures include small cationic (Methylene blue) and anionic (Methyl Orange) dyes but also bigger trianionic dyes with different geometries (see ESI for their corresponding molecular structure†). The amount of bound dye in dependence of concentration is easily quantified by UV-measurements of the

Table 1 Porous characteristics of the materials used as adsorbents

	BP	DCB1	DCB2
Total surface area ^a /m ² g ^{−1}	1625	1750	3270
Mesoporous surface area ^b /m ² g ^{−1}	1425	1020	2500
Total pore volume ^c /cm ³ g ^{−1}	2.42	1.58	2.4
Mesoporous pore volume ^b /cm ³ g ^{−1}	2.27	1.34	1.96
Average pore diameter ^b /nm	6.3	3.6	2.9

^a Determined by the BET method. ^b Determined from the NL-DFT pore size distribution. ^c Determined at $P/P_0 = 0.99$.

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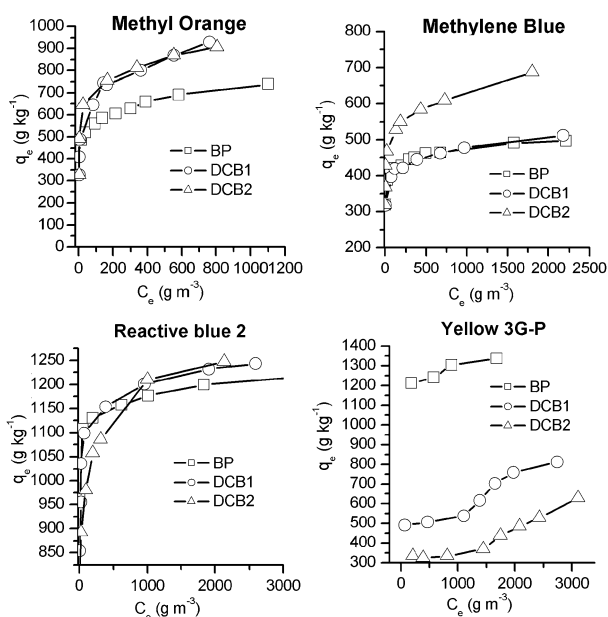


Fig. 1 Dye adsorption isotherms. q_e : equilibrium adsorption density, C_e : equilibrium concentration.

starting solution and the supernatant during the sorption experiment.

The adsorption kinetics are rather fast, the equilibrium being reached in less than 1 h. Decolouration of the supernatant is very efficient, as can be readily judged by the naked eye. To describe the data with a classical thermodynamic sorption model, the measurements were done after 24 h at 25 °C to ensure equilibrium. Even though these polymer frameworks are non-functionalized they can bind enormous amounts of dye into their pore structure, and values of up to 1300 mg g⁻¹ can be reached (Fig. 1). This is to be compared with activated carbons, which usually have values of 30–300 mg g⁻¹,^{12,13} while functional designer carbons optimized for the purpose of dye binding by electrostatic interactions between anionic dyes and cationic carbons can go up to 600–1100 mg g⁻¹.¹⁴ It is however to be stated that our polymer frameworks work for cationic and anionic dyes with about similar efficiency, *i.e.* the sorption is not charge-driven.

Table 2 Freundlich parameters of the adsorption isotherms^a

Dye	Polymer	Q_f	n	R^2
Methyl orange	BP	365	10.2	0.97793
	DCB1	440	9.3	0.97332
	DCB2	441	9.3	0.97601
Methylene blue	BP	316	16.8	0.99461
	DCB1	282	13.0	0.99047
	DCB2	351	11.6	0.99314
Reactive blue 2	BP	929	29.0	0.92836
	DCB1	832	18.4	0.93569
	DCB2	699	13.0	0.99228

^a From the Freundlich equation: $q_e = Q_f e^{1/n}$, where q_e is the equilibrium adsorption density, Q_f is the adsorption capacity and $1/n$ is the adsorption intensity. R^2 is the correlation coefficient.

As typical for sorption on carbon, the dye adsorption follows Freundlich isotherms, which can be used to quantify the binding curves, with the exception of Yellow 3G-P where the plots of the dye uptake against the equilibrium concentration shows some kind of two-step behaviour, more typical for cooperative binding.

The resulting fit parameters are summarized in Table 2.

The Q_f values quantify the adsorption strength and are in the upper range of typical sorption,¹² *i.e.* the triazine-based porous materials bind at least as strong as activated carbons. Experimentally, large specificities for each material/dye pair were found, and this chemical variation gives some extra information. For the smallest dye, methylene blue, the maximal amount of adsorbed dye indeed follows the surface area of the three polymer scaffolds, while Methyl Orange can differentiate between the DCB and the BP scaffolds, but not between the two DCB systems. For the bigger dyes, Reactive Blue 2 adsorption is balanced, *i.e.* the uptake of the dye is almost the same for all three materials (a fact we cannot explain), while for Yellow 3G-P, it is indeed the mesopore size that restricts the absolute capacity, and it is the sorbent with the largest pores (not with the highest surface area) which performs best.

Another advantage of a designed sorption material is the homogeneity of the chemical structure of its surface. Contrary to activated carbons, the point of zero adsorption enthalpy can therefore be quite precisely adjusted, *e.g.* by applying solvent mixtures. Indeed, the present materials could practically be completely recovered while leaching out the dye in an appropriate organic solvent, while binding was naturally performed from water. This way, sorption onto porous organic frameworks might become a powerful enrichment tool to recover organic molecules from their dilute solutions in water, enabling a loss-free solvent cycling as the key step of up-concentration.

To conclude, we have shown that carbonaceous polymer networks with hierarchical micro/mesopore structures represent sorption materials with superior capacity, binding strength, and sorption dynamics. As those systems are chemically uniform and chemically and thermally very stable, we expect their usefulness in a variety of advanced chemical processes.

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