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Rigid π-Extended Triptycenes via a Hexaketone Precursor

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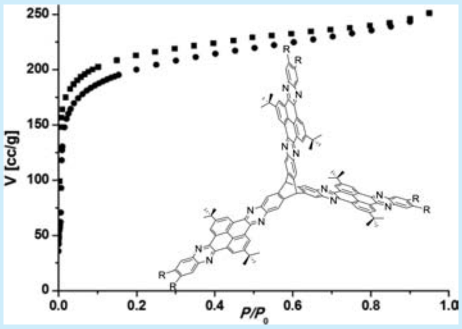
S *Supporting Information*

ABSTRACT: A high-yielding synthesis of a rigid hexaketone is presented that can be transformed into π-extended D_{3h}-symmetric triptycene derivatives with high internal molecular free volumes (IMFVs). The products show excellent photophysical properties combined with high specific surface areas.



Interest in porous materials derived from discrete molecules has increased in recent years because these materials bear the advantage of being soluble and therefore processable.[1,2] In principle, these discrete molecules can be divided into two subclasses, those with intrinsic molecular pores, such as organic cages,[3] cucurbiturils,[4] or calixarenes,[5] and those that do not have any molecular void or cavity, in consequence forming extrinsic pores in the solid state.[6] For the generation of extrinsic porous molecular materials two strategies have been proposed. One strategy is the synthesis of relatively small rigid molecules that self-assemble via strong directing intermolecular interactions, such as hydrogen bonding, enabling the formation of crystalline extrinsic porous materials with Brunauer–Emmett–Teller (BET) surface areas up to 2796 m^2/g.[7] The other possibility is the exploitation of internal molecular free volume (IMFV).[8] Rigid larger molecules can be constructed in such a way that it is impossible for those to pack efficiently, thus containing large IMFVs. McKeown and co-workers have demonstrated that phthalocyanines with bulky substituents form large pores in the crystalline state with accessible surface areas of approximately 1002 m^2/g.[9] Because of the IMFV of large extended molecules, the aggregation does not necessarily have to be highly ordered in a crystalline manner to achieve porosity, and frustrated packing in an amorphous phase also leads to highly porous material.[10]

McKeown et al. recently introduced the concept on constructing OMIMs (organic molecules of intrinsic microporosity) by using rigid building blocks derived from spiro bisfluorenes or triptycenes in a modular manner.[11−13] It is suggested by using the right combination of building blocks that in theory high specific surface areas of up to 2000 m^2/g should be accessible,[13] which to the best of our knowledge still has to be experimentally proven. For this class of molecules the highest BET surface areas (499 m^2/g) in the amorphous state were reported by Chong and MacLachlan for trinuclear triptycene nickel salphenes with large IMFVs.[14]

By enlarging the aromatic arms of the triptycene, the IMFVs can be increased, which has been demonstrated before.[15−17] Although these molecules contain large π-extended arms, they have not been considered yet as precursors for permanent porous materials.

Here, we present the synthesis of π-extended shape-persistent triptycene derivatives with large IMFVs, which are highly microporous in the solid state. Additionally, these molecules are good electron-acceptors as has been studied by photophysical measurements. This has not been realized for soluble porous molecules yet and opens up new possibilities to combine porosity with organic electronics.[18]

The synthesis is based on condensation reactions with the air-stable hexaammonium chloride salt **1** (Scheme 1).[19] To elongate the π-planes of the moieties, **1** was reacted with pyrene tetraketone **2**[20] in excess (18 equiv) to avoid any oligomer or polymer formation giving hexaketone **3** as a bright orange powder in high yields of 87%. As has been developed before, the free base of **1** is generated in situ by adding stoichiometric amounts (8 equiv) of potassium acetate to the reaction mixture.[19] The excess of tetraketone **2** was recovered by column chromatography (see the Supporting Information) and can be used again. Hexaketone **3** can further be transformed into the tris-quinoxalino[2′,3′:9,10]phenanthro[4,5-*abc*]-phenazines (tQPPs) **5a−e** in yields up to 79% by condensation with corresponding diamines **4a−e**.

Single crystals of **3** were grown from cooling a solution in hot *o*-dichlorobenzene to room temperature (Figure 1, for crystallographic details, see the Supporting Information). Besides CH−π interactions, π−π stacking is the major packing motif. In the crystal of **3**, two types of π−π stacking motifs can be distinguished. One type (type I in Figure 1 a) shows a parallel arrangement of the π-arms with a distance between the

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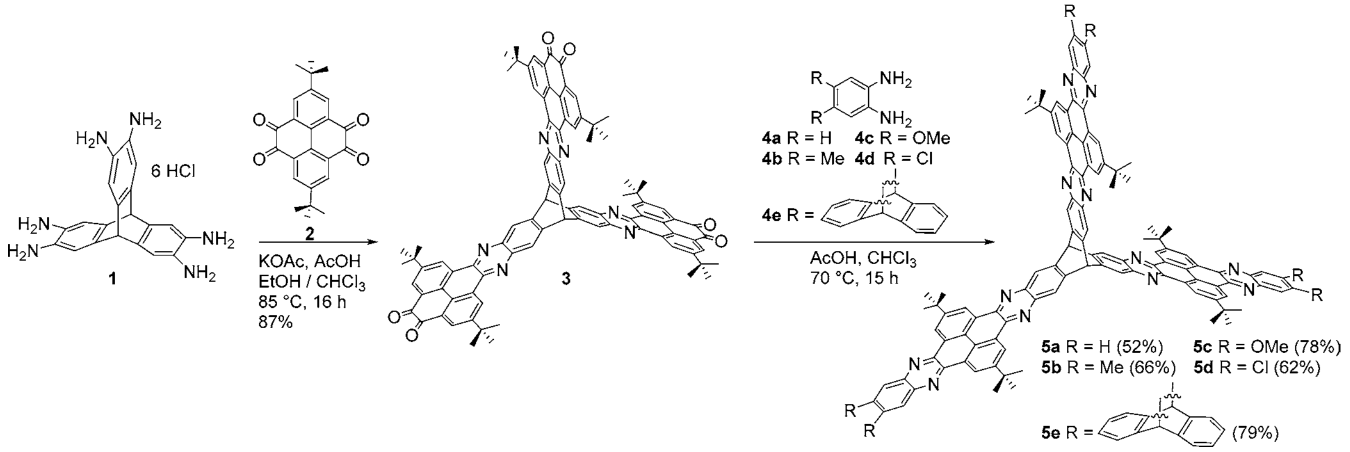
Scheme 1. Synthesis of Rigid π-Extended Triptycenes 5a−e[a]



[a]Note: For **5c** and **e**, the corresponding diammonium chloride salt **4′c** and **4′e** has been used to generate the free bases **4c** and **4e** in situ (for further details, see the Supporting Information).

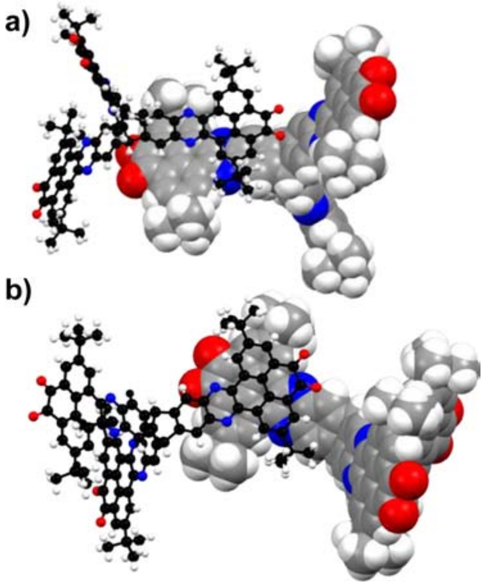


Figure 1. Two major packing motifs found in the crystalline state of **3**. (a) Type I with the parallel alignment of the elongated π-planes. (b) Motif type II with the nonparallel alignment of the elongated π-planes. Solvent molecules are omitted for clarity.

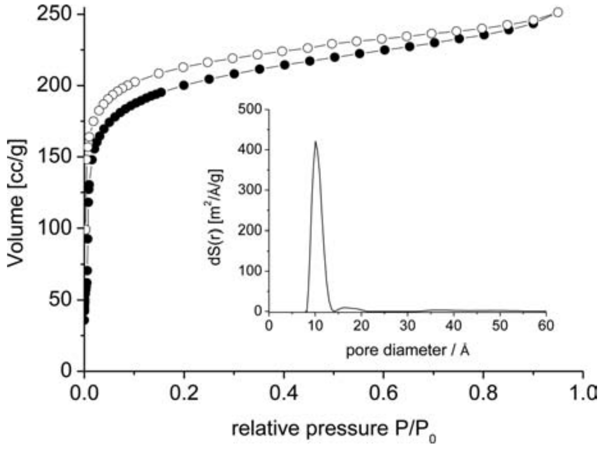


Figure 2. Nitrogen sorption isotherm of **5a** at 77 K: ●, adsorption; ○, desorption. Inset: pore size distribution calculated by QSDFT.

π-planes of approximately 3.3 Å.[21−23] The other type (type II, Figure 1 b) shows an orientation of approximately 130° of the two extended π-arms to each other, and a significantly longer distance of approximately 3.5 Å has been measured between those two units. To date, only planar π-extended systems containing this or similar molecular units have been described.[23]

It is expected that due to the high IMFVs of **5a−e**, the molecules should not be able to pack densely and form pores in the solid state. By nitrogen sorption measurement we found that all compounds form microporous materials with high specific surface areas. The isotherm for nonsubstituted compound **5a** is of type I with a small hysteresis (Figure 2) and a surface area of 754 m^2/g (BET model). The pore-size distribution by QSDFT (Quenched Solid Density Functional Theory, Kernel for N$_2$ on carbon at 77 K, slit/cylindrical pore)[24] had the smallest fitting error of 1.54% and shows a relative sharp maximum at 10 Å, which is a hint for some degree of order in the solid state. Indeed, powder X-ray diffraction of the as-synthesized and activated material showed a number of sharp peaks, revealing that the material contains a substantial amount of microcrystals. The other materials derived from periphery-substituted tQPPs **5b−e** show different isotherms with larger hysteresis between the adsorption and desorption branches (Supporting Information). Due to the hysteresis found, the pore-size distributions are not as pronounced and sharp as that of **5a** but show distinct maxima at approximately 10 Å (Supporting Information). Despite that, the calculated surface areas of **5b** and **5d** are slightly lower than for **5a** but higher than reported for other amorphous molecular materials with high IMFVs (see Table 1). The tQPP **5e** with triptycenylene units has a different peripheral molecular geometry than **5a−d**, which might result in a denser packing with a specific surface area of 293 m^2/g. The compound **5c** with methoxy groups in the periphery of the molecule shows also a substantial lower surface area, for which we have no explanation at the moment. Except **5a**, all other compounds are amorphous, as has been found by PXRD (Supporting Information).

QPPs are well-known electron acceptors and show typical photophysical and electrochemical properties, which have been studied with respect to organic electronics.[21−28] The

Table 1. Comparison of Photophysical Properties and Porosities

compd	λ_{abs}^{a,b} (nm)	λ_{abs}^{a,c} (nm)	λ_{em}^{a} (λ_{ex}) (nm)	ε ($M^{-1}\cdot cm^{-1}$) (nm)	$E_{g(opt)}$^{d} (eV)	SA_{BET}^{e} (m^2/g)	$SA_{Langmuir}$^{e} (m^2/g)	V^{f} (cm^3/g)	pore width^{f} (Å)
3	314	408		160700 (408)	2.4	nd	nd	nd	nd
5a	334	430	438 (344)	203700 (430)	2.8	754	867	0.342	10.0
5b	336	433	443 (346)	171200 (433)	2.8	553	650	0.419	10.5
5c	339	425	456 (349)	119100 (425)	2.7	206	240	0.142	10.0
5d	338	432	449 (348)	231000 (432)	2.8	517	614	0.352	10.0
5e	339	433	445 (349)	162000 (433)	2.8	293	350	0.191	10.0

[a]Measured in $CHCl_3$ at rt. [b]Absorption maximum at the shortest wavelength. [c]Absorption maximum at the longest wavelength. [d]Estimated from absorption onset. [e]N_2-sorption at 77 K with data points for P/P_0 between 0.01 and 0.1 for the BET surface and 0.02 and 0.1 for the Langmuir surface. [f]Calculated with QS-DFT-methods. nd, not determined.

hexaketone **3** shows a structured absorption spectrum with three maxima at λ_{max} = 314, 386, and 408 nm (Figure 3). Additionally a shoulder with lower intensity at 430 nm can be detected, which is assigned to the n–π^* transition. The UV/vis absorption spectra of all tQPPs **5a**–**e** have a pronounced and characteristic shape, comparable to planar QPPs.[25] For the nonsubstituted tQPP **5a**, two broad maxima with typical vibronic patterns can be found at λ_{max} = 334 and 430 nm, which can be assigned to π–π^* and n–π^* transitions.

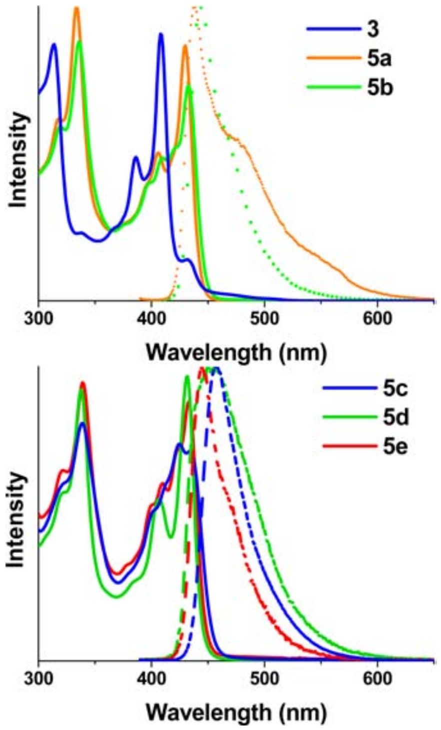


Figure 3. Normalized UV–vis absorption (chloroform, 6×10^{-6} M) and fluorescence (1×10^{-6} M, dotted lines) spectra of **3** and **5a**,**b** (top) and **5c**–**e** (bottom) in chloroform at room temperature.

Independently, whether excited at 430 nm or at 344 nm, compound **5a** showed a greenish blue fluorescence with an emission maximum at λ_{em} = 438 nm. The vibronic structure of the maxima as well as the relatively small Stokes shifts of 8 nm reveal that only small structural changes of the molecular scaffold occur during excitation.

The substituents in the periphery of the tQPPs do not influence the absorption properties very much. Independently, whether electron-withdrawing chloro (**5d**) or electron-donating methoxy substituents (**5c**) are attached, the maximum for both the π–π^* and n–π^* transitions shift less than 10 nm. The same is observed with the emission.

In conclusion, we have presented a facile synthetic access to nonplanar rigid molecular electron acceptors with large IMFVs forming micropores in the solid state with high surface areas and narrow pore-size distribution. The combination of these three material properties (solubility, light absorption/emitting and microporosity) is to the best of our knowledge not known and enables new applications in organic electronics or sensing,[2] which will be investigated by our group in more detail as well as further studies of the compounds in their crystalline states. The three-dimensional acceptor molecules have no literature precedent and will be studied as substitutes for C_{60} derivatives for bulk heterojunction organic photovoltaics.[29]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, gas sorption isotherms, NMR spectra, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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