Porous shape-persistent rylene imine cages with tunable optoelectronic properties and delayed fluorescence†

Hsin-Hua Huang, Kyung Seob Song, Alessandro Prescimone, Alexander Aster, Gabriel Cohen, Rajesh Mannancherry, Eric Vauthey, Ali Coskun* and Tomáš Šolomek*

A simultaneous combination of porosity and tunable optoelectronic properties, common in covalent organic frameworks, is rare in shape-persistent organic cages. Yet, organic cages offer important molecular advantages such as solubility and modularity. Herein, we report the synthesis of a series of chiral imine organic cages with three built-in rylene units by means of dynamic imine chemistry and we investigate their textural and optoelectronic properties. Thereby we demonstrate that the synthesized rylene cages can be reversibly reduced at accessible potentials, absorb from UV up to green light, are porous, and preferentially adsorb CO₂ over N₂ and CH₄ with a good selectivity. In addition, we discovered that the cage incorporating three perylene-3,4:9,10-bis(dicarboximide) units displays an efficient delayed fluorescence. Time-correlated single photon counting and transient absorption spectroscopy measurements suggest that the delayed fluorescence is likely a consequence of a reversible intracage charge-separation event. Rylene cages thus offer a promising platform that allows combining the porosity of processable materials and photochemical phenomena useful in diverse applications such as photocatalysis or energy storage.

Introduction

Shape-persistent organic cages opened up new possibilities to form various supramolecular hosts and porous materials with well-defined, tunable internal cavities. The porosity of organic cages originates from the presence of the internal cavity, which is responsible for the intrinsic porosity of the material along with other accessible pores that emanate from the extrinsic voids created through the packing of cage molecules in the solid-state. Unlike other porous materials such as zeolites, metal–organic frameworks (MOFs), covalent organic frameworks (COFs) and porous organic polymers, the solution processability of porous organic cages (POCs) represents an important advantage. It should, however, be noted that the packing of cage molecules has a profound impact on the porosity of POCs. For example, different polymorphs have been shown to result in different porosity. Similar to COFs, POCs are typically synthesized from highly preorganized organic building blocks via dynamic covalent chemistry utilizing reversible condensation and addition reactions or alkyne methathesis. The most prominent examples are the condensation reactions of boronic acids with alcohols and aldehydes with amines. This approach circumvents the problems of multi-step synthesis that relies on kinetically controlled reactions with low overall yields. Although the resulting structures are often not chemically stable, post-synthetic modification strategies to convert organic cages into stable materials have recently emerged. The porosity of some POCs has been shown to match that of COFs. Accordingly, POCs have been exploited in applications that rely on their porous nature, such as gas sorption and separation, molecular sieving, sensing, catalysis or transport of ions.

However, contrary to COFs, studies that explore the electronic properties of POCs are rather scarce. Yet, organic cages represent well-defined molecular architectures with building blocks arranged spatially with high precision, which is an important requirement for electronic materials. As a result, properties that typically arise from the interplay of the intermolecular electronic coupling between molecules in the solid-state could potentially emerge within a single cage due to its three-dimensional structure. Importantly, the incorporation of chromophores or redox-active molecules could also allow the investigation of their mutual electronic communication both in a solution or in the solid-state.
Two examples of POCs incorporating porphyrin moieties have recently been shown to exhibit interesting optoelectronic properties. Porphyrin boxes can possess relatively high Brunauer–Emmett–Teller (BET) surface areas (1370 m² g⁻¹) and show a good selectivity towards CO₂ over N₂ and CH₄. The ability to incorporate different metal centers into porphyrins transforms porphyrin POCs into promising heterogeneous CO₂ or O₂ reduction catalysts. The co-crystallization of a cubeshaped porphyrin cage with fullerene allows for a photoinduced charge-separation with a biphasic decay of the charge-separated state due to the anisotropy of the porphyrin–fullerene interaction that cannot be achieved in the co-crystals of fullerenes with monomeric porphyrin units. Recently, the first porphyrin heterogeneous POC photocatalyst has been reported. It generates singlet oxygen with high-efficiency and facilitates photo-oxidation of primary amines with conversion efficiencies >99% under visible light irradiation. Other examples of luminescent or diradicaloid organic cages also exist but they are accessed via kinetically controlled reactions or the porosity of these cages has not yet been determined.

We have recently reported the first example from a series of chiral imine organic cages (Scheme 1) with built-in redox-active rylene units. Cage 1a is composed of three naphthalene-1,4:5,8-bis(dicarboximide)s (NDIs), a well-known electron acceptor, which endowed 1a with unique optoelectronic properties such as the ability to store up to six electrons, intracage electron hopping and photoinduced charge-separation with prolonged excited state lifetimes. Encouraged by these initial results, herein, we explore the structural variability of rylene cages and complete the series by the synthesis of 1c. The therodynamic control of imine formation demands that the starting compounds are soluble to drive the equilibrium to the products. We therefore tried to synthesize 1a in dry chloroform, in which the diamines 2 possess a sufficient solubility. We observed a full conversion and a clean formation of 1a in 72 hours at 80 °C in 60% yield after purification by HPLC. It suggests that 1a is the thermodynamic product in chloroform. The PMDI cage 1b was then synthesized from 2b formed in situ from its ditosyl salt, which allowed an easier handling and synthesis, in the presence of excess triethylamine in 62% yield after purification. Finally, PDI cage 1c was prepared from 2c in 18% yield. The three-dimensional shape of the cages improved their solubility in chlorinated solvents, THF, toluene or nitrobenzene when compared to simple PMDI, NDI, and PDI derivatives with cyclohexyls in imide positions. However, cage 1c possesses the lowest solubility in the series, which complicated its purification and affected the isolated yield. The structure of cages 1 was confirmed by ¹H, ¹³C and 2D homo- and heteronuclear correlation NMR spectroscopy, HR-ESI mass spectrometry (see the ESI†) and single crystal X-ray diffraction analysis (XRD, vide infra).

Enantiopure samples of (RRR)- or (SSS)-1 are obtained when the synthesis commences from enantiopure diamines 2 as evidenced by the mirror images of the circular dichroism spectra of each pair of enantiomers (Fig. 1 and S45†). The Cotton effects with the zero-crossing are located at the absorption maxima in measured steady-state optical spectra, quantum yields, time-correlated single photon counting, transient absorption, and electrochemical data suggest that photoexcited cage 1c undergoes a reversible intra-cage charge separation between two PDI units. Moreover, we also explored the porosity and affinity of these cages towards small gases. Notably, we showed that rylene cages are porous and possess a good CO₂ selectivity over N₂ and CH₄. The interplay between the textural and electronic properties of these cages could pave the way for the development of highly efficient porous photocatalysts or optoelectronic materials.

Results and discussion

Synthesis and properties

The structure of the cages 1 requires that a ditopic amine and a tritopic aldehyde react in a [3 + 2] condensation reaction (Scheme 1). Previously, we synthesized 1a by refluxing the diamine 2a with benzene-1,3,5-tricarbaldehyde in toluene under Dean–Stark conditions. However, this approach was not suitable for the synthesis of 1c because the corresponding diamine 2c has a very low solubility in toluene. Although, the cage formation could be detected by MALDI-TOF, a majority of impure samples. Generally, PDI s have a lower solubility compared to the NDI or PMDI derivatives. Therefore, we performed DFT calculations to estimate the relative stabilities of 1b and 1c using an isodesmic reaction shown in Scheme S1† prior to the synthesis. We found that all cages display similar stability (Table S1†) even when the solvent environment was included, which promised a successful synthesis of 1b and 1c. The thermodynamic control of imine formation demands that the starting compounds are soluble to drive the equilibrium to the products. We therefore tried to synthesize 1a in dry chloroform, in which the diamines 2 possess a sufficient solubility. We observed a full conversion and a clean formation of 1a in 72 hours at 80 °C in 60% yield after purification by HPLC. It suggests that 1a is the thermodynamic product in chloroform.
ESI unequivocally con

We were able to grow single crystals of rylene cages

Solid-state structure

determinate. The cages crystallize in a monoclinic space group

1a and 1c. This reveals a chiral exciton coupling between the

chromophores due to the helical twist of the cage structure,

which is absent in 3a and 3c (Fig. S47†). The Cotton effect in

the visible absorption range of the PDI’s S0–S1 transition (λmax = 522 nm) in 1c is markedly stronger than that observed for the

structurally similar 1a (λmax = 381 nm). The center-to-center

and the edge-to-edge distances (DFT, Fig. 2a) between two

rylene units are shorter in 1c than in 1a by ≈ 0.2–0.4 Å. This,

together with the higher oscillator strength of the PDI, results in

a stronger exciton coupling in 1c. Further evidence is provided

by UV-Vis absorption spectra that show clearly that the change

in the ratio of the intensities of the individual vibronic bands

with respect to monomeric reference compounds 3 is larger for

1c than for 1a (Fig. 1). The Rabs, the ratio of the oscillator

strengths of the first and the second vibronic bands, I0/If0, decreases to 1.13 in 1c and to 1.08 in 1a from 1.65 and 1.21 found in 3c and 3a, respectively. Despite an increase in the

long-range Coulomb coupling, the short-range charge-transfer

coupling is small and it does not manifest in the electro-

chemical measurements in CH2Cl2. In each cage 1, no splitting

in the first or the second reduction wave can be observed in the

cyclic voltammograms [see the ESI†]. As in 1a,3a each cathodic

wave in both 1b and 1c corresponds to an electron transfer event

that involves three electrons.

Solid-state structure

We were able to grow single crystals of rylene cages 1 and we

unequivocally confirmed their structures. We obtained crystals

of 1b and 1c by a slow diffusion of methanol vapors into

nitrobenzene solutions of (RRR)- or (SSS)-1b and 1c, respectively.
The cages crystallize in a monoclinic space group C2 (see the

ESI†) unlike 1a that crystallizes from the same solvent in an

orthorhombic C2221 space group.42 Fig. 2 compares the single

crystal XRD solid-state superstructures of all cages. The

symmetry of individual cages in the crystal structure decreases

compared to the models obtained from DFT calculations, which

predict that the lowest energy geometries of all cages 1 possess

a D3 symmetry in agreement with their NMR spectra. The

structural distortion due to packing must be accompanied by an

energy penalty. We estimated this energy by DFT calculations

where the crystal structure geometries were partially optimized

by fully relaxing the coordinates of all hydrogens and the bond

lengths between the heavy atoms (C, O, N). The calculated

energies (Table S3†) suggest that the cages are rather flexible in

a solution and sample the conformational space faster than the

NMR time scale at room temperature. Each rylene cage displays

an analogous packing (Fig. 2, side view) with the individual

molecules assembled into a series of columns. These columns

are mutually displaced by a similar length in 1a and 1b, which

have a comparable aspect ratio, while the displacement

increased in 1c as a result of its elongated structure. The solvent

molecules fill both intrinsic and extrinsic voids in all crystal

structures. The latter consists of the pockets created by six

cyclohexanediyl and two tris(mininomethyl)-benzene units, i.e.,
pockets between two bridging units of a pair of cages in a column. The larger aspect ratio of 1c allows for a different

rylene–rylene interaction and affects the packing as can be

observed when the solid-state superstructure is investigated

from a different perspective (Fig. 2, top view). In cages 1a and

1b, the edge-to-face NDI–NDI and PMDI–PMDI interaction
leads to blocking of window-to-window packing between the cages, which partially closes the intrinsic voids. On the contrary, no edge-to-face orientation of PDI units is present in 1c. Instead, prismatic columns with a slipped stack of tilted PDI units pervade the crystal structure. Consequently, a full window-to-window packing is permitted creating a new hexagonal extrinsic void, orthogonal to the now fully accessible intrinsic voids.

For other solvents, however, the quality of the single crystal X-ray diffraction data exhibited a significant disorder irrespective of the measurement temperature because of the residual solvent molecules. This allowed us to confirm the structure of the cage and the unit cell of the crystal in such cases but with a worse resolution of the individual cage structure (1b, toluene: R1 = 18%; 1c, nitrobenzene: R1 = 14%). Comparison of the crystal structures obtained from nitrobenzene and toluene reveals that the electronic nature of the solvent molecules determines the molecular packing. An electron rich guest, such as toluene, prefers to be incorporated in the cavity of the cage, while nitrobenzene of similar size is held less tightly (Fig. S58†). This phenomenon is observed for both 1a and 1b, although the electron affinity of PMDI is markedly lower than that of NDI (Table S2†). This generally allows controlling the solid-state morphology by host–guest interactions in rylene cages 1. The absence of a strong host–guest interaction between nitrobenzene and the rylene cage results in crystal structures that possess both intrinsic and extrinsic voids. Therefore, we decided to grow single crystals from THF, a solvent that is expected to have no appreciable host–guest interaction with the rylene but with a much lower boiling point than nitrobenzene. Despite the large size and a good quality of the single crystals that we obtained for 1a and 1b by crystallization from THF, a very poor diffusion could only be observed at wide angles, which prevented us from acquiring sufficient data and resolving the crystal structure in this case.

**Gas adsorption and porosity**

The presence of both intrinsic and extrinsic voids in the crystal structures of 1 motivated us to explore the porosity of the cages. Only cages 1a and 1b could be synthesized in a large enough quantity to perform these studies. Initial gas sorption analysis using Ar or N2 at 77 K with samples obtained from nitrobenzene displayed a low porosity (Fig. S60†). We attribute this result to the residual nitrobenzene molecules blocking the voids even after the activation of the samples under dynamic vacuum at 120 °C for 24 h because of the high boiling point of nitrobenzene (Fig. S64†). We reasoned that the cages crystallized from THF would allow us to remove the solvent molecules from the pores more effectively. Indeed, we observed a significant increase in the BET surface areas (Fig. 3 and S60†). Cage 1a showed a characteristic type I gas adsorption profile, an indication for a highly microporous structure, with a BET surface area of 522 m² g⁻¹ (Table 1). Further analysis of the adsorption isotherm revealed that the micropores and external pores are responsible for ≈ 60% and ≈ 40% of the total BET surface area, respectively. Interestingly, we observed almost no N2 uptake at low relative pressures for the PMDI cage 1b until the pressure reached a value of p/p0 ≈ 0.35, at which point a fast uptake of N2 occurred. Therefore, the BET surface area could not be quantified in this case. In addition, we observed a non-closed desorption isotherm without mesopore hysteresis for 1b. The behavior of 1b thus points to a gate opening phenomenon related to kinetic gas trapping, which is generally observed for soft porous crystals and flexible porous cages.† The empty voids in the activated material are initially closed at low pressures at 77 K and a necessary structural rearrangement is achieved only with increasing the external pressure to a point when a gate opening takes place. This was accompanied by a substantial increase in the pore volume (0.34 cm³ g⁻¹, Table 1). We observed this gate opening phenomenon also for Ar adsorption isotherms at 77 K (Fig. S60†). We speculate that the difference between the N2 adsorption behavior of 1a and 1b originates from the intrinsic flexibility of these cages. Whereas 1b adopts a closed-form at low pressures due to its flexibility,‡ it can transform into an open-form once the threshold pressure (p/p0 = 0.35) is reached. However, 1a displayed a shape-persistent adsorption due to the limited rotation of the NDI linker in the solid-state. This is supported by the difference in barriers of rotation around the imidic C–N bond in models of NDI and PMDI obtained by DFT calculations (ΔE ≈ 11 kcal mol⁻¹, Table S11†).

In order to probe the affinity of small gases towards the cages, we performed CO2, CH4 and N2 gas uptake experiments at 273, 298 and 323 K up to 1 bar (Fig. 3, S61, S62 and Tables
S4, S5†). Both cages 1a and 1b showed higher affinity towards CO2 with a similar isosteric binding enthalpy (Q_{eq}) of \(\approx 27\) kJ mol\(^{-1}\) at zero coverage and a relatively high CO2 uptake capacities of 2.91 and 2.00 mmol g\(^{-1}\), respectively, at 273 K and 1 bar (for comparison with other POCs, see Table S6†). The N2 uptake capacities of 1a and 1b are 0.31 and 0.16 mmol g\(^{-1}\) (273 K, 1 bar), respectively. The high CO2 affinity of the cages prompted us to calculate the CO2/N2 selectivity using ideal adsorbed solution theory (IAST), which is used to determine the selectivity for binary gas mixtures using the experimental pure gas isotherms. Cages 1a and 1b exhibited good IAST CO2/N2 selectivities of 26.9 and 45.5 (Fig. S61 and Table S4†), respectively. We also observed a good affinity towards CH4 with uptake capacities (Fig. S62 and Table S5†) of 1.09 and 0.65 mmol g\(^{-1}\) (273 K, 1 bar) and Q_{st} values of 21.6 and 22.6 kJ mol\(^{-1}\) for 1a and 1b, respectively, which is expected due to the hydrophobic nature of the cage cavity. Considering the rich chemistry of rylene diimides, one can imagine that their functionalization along the aromatic core to introduce heteroatoms could further boost the CO2 uptake capacities. Therefore, rylene cages provide a versatile platform, wherein the porosity, electronic properties, and chemical functionality could be tuned simultaneously to improve the gas uptake and selectivity.

**Excited-state behavior and delayed fluorescence in 1c**

The presence of three PDI units in the structure of 1c endows the cage with bright photoluminescence. A close inspection of the excited state properties of 1c, however, reveals a different excited-state behavior than that observed for monomeric PDI diimine 3c. The absorption and fluorescence spectra of 1c and 3c are similar (Fig. 1) and do not display solvatochromism in solvents of different polarity such as toluene, CH2Cl2, and benzonitrile (Fig. S43 and S44†). However, the fluorescence quantum yield (\(\Phi_{\text{em}}\)) of 1c decreases with increasing polarity of the solvent unlike in 3c, for which both the measured quantum yields (\(\Phi_{\text{em}} = 0.89\)–0.86, Table S7†) and the excited state lifetimes (\(\tau \approx 4\) ns, Table S8†) are insensitive.

The time-correlated single photon counting (TCSPC) data (Fig. 4 and Tables S7, S8†) show clearly that \(\tau\) of excited 1c in toluene is longer than that of 3c and it increases further in CH2Cl2. This result is surprising because a presence of an additional non-radiative process typically leads to a decrease of both the fluorescence quantum yield and the lifetime of the excited state. This contradiction is resolved by the analysis of the fluorescence kinetics of 1c in benzonitrile. The data show clearly a biexponential emission signal decay with a prompt and a delayed component with the lifetimes \(\tau_{\text{prompt}} = 1.10\) ns and \(\tau_{\text{delayed}} = 55.9\) ns, respectively. In fact, the analysis of the TCSPC data collected for 1c in toluene and CH2Cl2 (Fig. 4, inset) reveals that biexponential decay is already present in the latter. While \(\tau = 6.27\) ns in toluene, the \(\tau_{\text{prompt}} = 3.0\) ns and \(\tau_{\text{delayed}} = 10.2\) ns in CH2Cl2. Emission detected at the maximum of each vibronic band provided the same kinetic data. A ten-fold increase in the concentration did not affect either the measured \(\Phi_{\text{em}}\) or \(\tau\) of photoexcited 1c excluding the involvement of bimolecular processes. Although we could not acquire the individual prompt and delayed emission spectra, the determined quantum yields and the kinetic data for 1c in benzonitrile show that the prompt and the delayed fluorescence contribute comparably to the overall emission (see below). Because the steady-state optical spectra of 1c and 3c are alike in all the studied solvents, we concluded that the prompt and the delayed fluorescence emanate from the same emissive species in 1c, i.e., from an excited state localized on a single PDI unit (S\(_1\) state, Scheme 2). Therefore, a new process, absent in 3c, exists in 1c and equilibrates the emissive and a non-emissive excited state that we

| Cage | BET\(^a\) (m\(^2\) g\(^{-1}\)) | \(S_{\text{micro}}\) \(^b\) (m\(^2\) g\(^{-1}\)) | \(S_{\text{tot}}\) \(^c\) (m\(^2\) g\(^{-1}\)) | \(V_{\text{total}}\) \(^d\) (cm\(^3\) g\(^{-1}\)) | \(V_{\text{micro}}\) \(^e\) (cm\(^3\) g\(^{-1}\)) | \(V_{\text{ext}}\) \(^f\) (cm\(^3\) g\(^{-1}\)) | \(n_{\text{CO}_2}\) \(^e\) (mmol g\(^{-1}\)) | \(n_{\text{N}_2}\) \(^e\) (mmol g\(^{-1}\)) | \(Q_{\text{st}}\) \(^h\) | CO2/N2 \(^j\) |
|------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------
| 1a   | 522             | 312             | 210             | 0.44            | 0.2             | 0.24            | 0.31            | 2.91            | 21.6            | 27.0            | 26.9            |
| 1b   | 0               | 312             | 210             | 0.34            | 0.14            | 0.20            | 0.16            | 2.00            | 27.5            | 45.5            |

\(^a\) Brunauer–Emmett–Teller (BET) surface area calculated over the pressure range \((p/p_0)\) of 0.01–0.11. \(^b\) Micropore surface area calculated using the t-plot method. \(^c\) \(S_{\text{tot}} = S_{\text{total}} - S_{\text{micro}}.\) \(^d\) Total pore volume obtained at \((p/p_0) = 0.99.\) \(^e\) Micropore volume calculated using the t-plot method. \(^f\) \(V_{\text{ext}} = V_{\text{total}} - V_{\text{micro}}.\) \(^g\) Gas uptake (1 bar, 273 K). \(^h\) At zero coverage. \(^i\) Selectivity (IAST, 273 K) of CO2 over N2 adsorption. \(^j\) Not available.

Table 2 Photophysical parameters determined for samples of 1c in toluene, CH2Cl2, and benzonitrile

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Toluene</th>
<th>CH2Cl2</th>
<th>Benzonitrile</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Phi_{\text{em}}) (^a)</td>
<td>0.83</td>
<td>0.75</td>
<td>0.40</td>
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<tr>
<td>(\tau_{\text{prompt}}) (^b) (ns)</td>
<td>6.27</td>
<td>3.00</td>
<td>1.10</td>
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<tr>
<td>(\tau_{\text{delayed}}) (^b) (ns)</td>
<td>–</td>
<td>–</td>
<td>55.9</td>
</tr>
<tr>
<td>(k_{\text{proc}}) (^c) (10(^{12}) s(^{-1}))</td>
<td>–</td>
<td>–</td>
<td>7.14</td>
</tr>
<tr>
<td>(\Phi_{\text{em}}) (^e)</td>
<td>–</td>
<td>–</td>
<td>0.52</td>
</tr>
<tr>
<td>(\Phi_{\text{prompt}}) (^e)</td>
<td>–</td>
<td>–</td>
<td>0.40</td>
</tr>
<tr>
<td>(\Phi_{\text{delayed}}) (^e)</td>
<td>–</td>
<td>–</td>
<td>0.45</td>
</tr>
<tr>
<td>(k_{\text{proc}}) (^′) (^d) (10(^{5}) s(^{-1}))</td>
<td>–</td>
<td>–</td>
<td>16.70</td>
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<tr>
<td>(\Delta G_{\text{proc}}) (^h) (kcal mol(^{-1}))</td>
<td>–</td>
<td>–</td>
<td>–0.02</td>
</tr>
<tr>
<td>(J_{\text{COAL}}) (^i) (cm(^{-1}))</td>
<td>265</td>
<td>69</td>
<td>25</td>
</tr>
<tr>
<td>(\Delta G_{\text{COAL}}) (^i) (kcal mol(^{-1}))</td>
<td>–</td>
<td>–</td>
<td>–7.10</td>
</tr>
</tbody>
</table>

\(^a\) Quantum yield of emission (see Table S7). \(^b\) Excited state lifetime from the prompt fluorescence signal decay (see Table S8). \(^c\) Excited state lifetime from the delayed fluorescence signal decay. \(^d\) \(S_0 \rightarrow S_1\) rate constant. \(^e\) Quantum yield of \(S_1 \rightarrow S_0\) process. \(^f\) Quantum yield of prompt fluorescence. \(^g\) Quantum yield of delayed fluorescence. \(^h\) \(S_0 \rightarrow S_1\) rate constant. \(^i\) Gibb's free energy of the \(S_1 \rightleftharpoons S_0\) equilibrium. \(^j\) Long-range Coulomb coupling calculated from eqn (4). \(^k\) Gibb's free energy of the PDI–PDI photoinduced electron transfer calculated from eqn (4).
the solvent polarity. Thus, \( k_{\text{proc}} = 75.0 \times 10^7 \text{ s}^{-1} \) (Scheme 2) can be calculated directly from \( \tau_{\text{prompt}} \) considering \( k_{\text{rad}} = 13.2 \times 10^7 \text{ s}^{-1} \) and \( k_{\text{nr}} = 2.71 \times 10^7 \text{ s}^{-1} \) that we determined from \( \tau \) and \( \Phi_{\text{em}} \) of 1c in toluene (Table 2). The quantum yield of the forward process \( \Phi_{\text{proc}} \) is given by eqn (1):

\[
\Phi_{\text{proc}} = \frac{k_{\text{proc}}}{k_{\text{proc}} + k_{\text{rad}} + k_{\text{nr}}} = k_{\text{proc}} \times \tau_{\text{prompt}}
\]

where \( \Phi_{\text{proc}} \) represents the excited state population initially transferred from \( S_1 \) to \( S^\ddagger \). In benzonitrile, \( \Phi_{\text{proc}} = 0.82 \). As a result, the \( \Phi_{\text{prompt}} \) of the prompt fluorescence can be obtained from \( (1 - \Phi_{\text{proc}}) \) and \( \Phi_{\text{delayed}} \) of the delayed fluorescence from \( (\Phi_{\text{em}} - \Phi_{\text{prompt}}) \). Their values in benzonitrile (Table 2), after correction for the non-radiative decay of the \( S_1 \) state, are \( \Phi_{\text{prompt}} = 0.15 \) and \( \Phi_{\text{delayed}} = 0.25 \), respectively. Clearly, prompt fluorescence is responsible for less than half of the overall luminescence quantum yield (\( \Phi_{\text{em}} = 0.40 \)). It follows that \( \Phi_{\text{delayed}} \) represents the total excited state population in the \( S^\ddagger \) state that decays radiatively by repopulating the bright \( S_1 \) state. There must be other deactivation channels from the \( S^\ddagger \) state that account for \( \approx 50\% \) of the quenching of the initially excited cage. Considering the individual quantum yields and the value of \( \tau_{\text{delayed}} \), the corresponding rate constant for the reverse process, \( k_{-\text{proc}} \), that repopulates the \( S_1 \) state could be derived\(^{16,18} \) according to eqn (2):

\[
k_{-\text{proc}} = \frac{\Phi_{\text{delayed}}}{\Phi_{\text{prompt}}} \times \frac{k_{\text{prompt}} k_{-\text{delayed}}}{k_{\text{proc}}}
\]

where \( k_{\text{prompt}} \) and \( k_{\text{delayed}} \) are the observed rate constants that correspond to the experimentally determined lifetimes \( \tau_{\text{prompt}} \) and \( \tau_{\text{delayed}} \), respectively. The calculated values of \( k_{-\text{proc}} \) in benzonitrile and 1c are listed in Table 2. The rate constants of the forward and the reverse process in the \( S_1 \rightleftharpoons S^\ddagger \) equilibrium provide an apparent equilibrium constant in benzonitrile \( K = 19.8 \) and the corresponding Gibbs free energy of \( \Delta G_{\text{proc}} = -1.77 \text{ kcal mol}^{-1} \) at 298 K (Table 2). The same line of arguments gives \( \Delta G_{\text{proc}} = -0.02 \text{ kcal mol}^{-1} \) at 298 K in CH2Cl2. Note, however, that the difference between \( k_{\text{proc}} \) and \( k_{-\text{proc}} \), which forms the basis of our kinetic analysis, is small in CH2Cl2 and, as a consequence, provides a less accurate value for the energy difference between the \( S_1 \) and \( S^\ddagger \) states in this solvent.

Although fluorescent organic cages were previously reported,\(^{18} \) cage 1c represents the first example of a covalent organic cage that displays a delayed fluorescence. This demonstrates the unique interplay of the PDI chromophores in its structure that promotes an unusual but very useful property that is typically observed in compounds with very different structural design incorporating twisted electron donor and acceptor motifs. For example, compounds with delayed fluorescence are important light-emitting materials used in organic light-emitting diodes.\(^{24} \) What is, however, the likely nature of the new non-emissive \( S^\ddagger \) state and the process by which it forms? There are three feasible scenarios to consider: (a) a formation of an excimer or an intramolecular H-type aggregate, (b) multie exciton generation, or (c) intracage charge-separation.
Formation of an excimer or an intramolecular H-type aggregate

A large electronic coupling is necessary between PDI units to form an excimer. This typically requires a cofacial orientation of the PDIs with a short intermolecular distance that can be achieved by a structural rearrangement in the solution. As a result, the excimer state, \(^{(1)}\text{[PDI-PDI]},\) may display enhanced excited state lifetime, a diminished fluorescence quantum yield and a partial charge-transfer (CT) character but it shows a markedly displaced and featureless fluorescence spectrum. There is no sign of an excimer emission in the steady-state fluorescence spectrum of 1c in any solvent. The distance of the PDI units in the DFT optimized structure of 1c (Fig. 2a) is too large to allow a sufficient coupling to form an excimer. In addition, the structural rearrangement would require the PDIs in the cage to rotate significantly (>30°) around the N-C bond connecting the PDI and the cyclohexyl connector to adopt a cofacial geometry. This rotation is, however, hindered and slow even on the NMR time scale because we observed four doublets for the PDI aromatic core protons in the \(^1\text{H} \text{NMR} \) of 1c at room temperature (Fig. S8†).

A comparison of the absorption spectra reveals that absorption maxima of 1c are slightly blue-shifted compared to the spectra of the monomeric 3c. The relative intensities of the individual vibronic bands also deviate as already discussed above. The ratio of the oscillator strengths of the first and the second vibronic bands, \(I_{0.0}/I_{0.1},\) decreases from 1.65 in 3c to 1.13 in 1c (Fig. 1), suggesting the presence of an H-type coupling in 1c.† Its magnitude is, however, small and can be estimated assuming a point-dipole interaction between transition dipole moments of two PDIs:

\[
J_{\text{Coal}} = \left| \mu_{0-1} \right|^2 \frac{1}{4 \pi r_{12}^3} \cos \varphi
\]

In this expression, \(\mu_{0-1}\) is the transition dipole moment \((3.50 \times 10^{-29} \text{ Cm, Table S9})\) that is parallel with the long PDI axis, \(r\) is the absolute solvent permittivity, \(r_{12}\) is the center-to-center PDI–PDI distance \((9.62 \AA, \text{Fig. 2})\) obtained from the DFT-optimized geometry of 1c, and \(\varphi\) is the tilt angle between the two PDIs in the cage \((\approx 10^\circ).\) In CH\(_2\)Cl\(_2\), we obtain an interaction energy \(J_{\text{Coal}} = 69 \text{ cm}^{-1}\) that agrees well with \(J_{\text{Coal}} = 70 \text{ cm}^{-1}\) calculated from the vibronic bands intensity ratio \(R_{\text{abs}}\) according to Spano and co-workers.\(^{26}\) Our TD-DFT calculations predict a somewhat higher coupling \((\approx 180 \text{ cm}^{-1}, \text{Table S9})\). Both the experiment and theory show that \(J_{\text{Coal}}\) does not vary correctly with the solvent polarity (Table 2) and, therefore, is inconsistent with the excited state behavior that we observe for samples of 1c in different solvents. In addition, rapid excited state symmetry-breaking is induced by solvent field (polar medium) or structural (non-polar medium) fluctuations when the interchromophore coupling is very small and, therefore, the exciton must quickly localize on a single PDI unit in 1c. Nevertheless, the presence of this small coupling is sufficient to reduce the \(k_{\text{rad}}\) and \(\Phi_{\text{em}}\) in 1c (toluene, Table 2) when compared to 3c in the three studied solvents (Tables S7 and S8†).

Intracage charge-separation (CS) and multiexciton (ME) generation

Rylene diimides are known as excellent electron acceptors in their ground or excited states. We reported previously\(^{30}\) that 1b serves as a strong oxidant and transfers an electron from the tris(iminomethyl)benzene bridge on an ultrafast time scale when excited with UV light. NDIs and PDIs have similar redox potentials but the excited state of 1c has a considerably lower energy than that of 1a (Table S2†). Indeed, we do not observe quenching of fluorescence in 3c, which confirms that the tris(iminomethyl)benzene bridge is electrochemically innocent in the excited 1c. However, an initially delocalized exciton in PDI dimers or higher aggregates is known\(^{26}\) to undergo a symmetry-breaking CS when two PDIs disproportionate to a pair of radical ions, PDI+ and PDI−. Recombination of these radical ions might repopulate the bright singlet excited state and result in a delayed fluorescence.

A kinetically equivalent event involves formation of a rather exotic species, a ME state, which is an intermediate in a process called singlet fission.\(^{29}\) Singlet fission has attracted considerable interest of scientific community in recent years because the incorporation of singlet fission compounds into solar cells could raise their theoretical efficiency limit. In a singlet fission, an excited singlet state transforms into a correlated triplet pair, the ME state, with an overall singlet spin character. Its fate in molecular dimers/oligomers is typically twofold, (a) it splits into two independent triplet states if the process is exergonic or (b) it recombines back to the excited singlet state.\(^{29}\) Both processes can lead to a delayed fluorescence. The former via a triplet-triplet annihilation (TTA) with a rate comparable to the lifetime of an independent triplet state, while the latter with lifetimes typically in nanoseconds. Singlet fission has been observed in solid samples of PDI derivatives.\(^{29}\) A strong electronic coupling in cofacial PDI dimers typically leads to the formation of unproductive excimer\(^{22}\) or charge-separated states\(^{28,23}\) and a slipped stack geometry, observed in PDI thin films, is believed\(^{15}\) to be crucial for a singlet fission to occur in PDI derivatives. Very recently, Hong et al. proposed\(^{34}\) that the singlet fission can occur also in PDI dimers in solution. The dimers displayed two distinct fluorescence lifetimes in 1,1,2,2-tetrachloroethane but the longer lifetime was attributed to the emission of an excimer state.\(^{14}\) The dimers exhibited a strong \(J_{\text{Coal}} (>500 \text{ cm}^{-1})\) and a short-range CT coupling of a similar magnitude but of the opposite sign \((J_{\text{CT}} < -500 \text{ cm}^{-1})\). The ME generation process occurred with \(t_{\text{ME}} = 370\) and 20 ps in toluene and benzonitrile, respectively, after an initial structural or solvent reorganization enhancing the CT character in the excited dimers. The results corroborate the CT-mediated singlet fission mechanism observed previously in structurally related terylene diimides (TDIs).\(^{25}\)

The CS and ME generation can both be described by the diagram in Scheme 2 and they are, therefore, kinetically indistinguishable. The former process may be facile only when the corresponding Gibbs free energy of the photoinduced electron transfer, \(\Delta G_{\text{CS}}\), is negative. To quantify the \(\Delta G_{\text{CS}}\) for 1c, we applied eqn (4).\(^{26}\)
\[ \Delta G_{\text{CS}} = e \times \left[ E_{\text{ox}} - E_{\text{red}} \right] - E_{0-0} - \frac{e^2}{4\pi\varepsilon_{\text{r}}\varepsilon_{0}} \]  

(4)

where \( E_{\text{ox}} \) and \( E_{\text{red}} \) are the first oxidation and reduction potentials, respectively, \( E_{0-0} \) is the excited state energy, and \( e \) and \( \varepsilon_{\text{r}} \) are as described above. We obtained the redox potentials and the excited state energies by cyclic voltammetry\(^\text{37} \) and optical spectroscopy (Table S2†), respectively. The resulting Gibbs free energy of the electron transfer in CH\(_2\)Cl\(_2\) is \( \Delta G_{\text{CS}} = -7.10 \) kcal mol\(^{-1}\) at 298 K. The value of \( \Delta G_{\text{CS}} = -8.92 \) kcal mol\(^{-1}\) is obtained for the electron transfer in polar benzonitrile by correcting the redox potentials with solvation energies calculated by DFT (Table S10†). Both values are negative and predict a productive charge separation event. The \( \Delta G_{\text{proc}} \) determined from the kinetic data is, however, considerably higher, even if the last term in eqn (4) was ignored. In fact, the calculated \( \Delta G_{\text{CS}} \) values suggest that the electron transfer is too exergonic to allow efficient charge recombination to repopulate the bright S\(_1\) state on the observed time scale. In such a case, a charge-separated state typically decays rapidly to the ground or to a triplet state, \( ^3\text{Ic} \). This was observed previously in a macrocycle with weakly coupled PDIs\(^\text{38} \) or in 1a.\(^\text{19} \) No delayed emission was detected in the former case and the charge recombination was rapid in the latter. In addition, electrogenerated chemiluminescence that was observed in PDI derivatives in CHCl\(_3\)/CH\(_3\)CN solvent mixture by Bard and co-workers\(^\text{38} \) showed that the population of the emissive excited state occurred exclusively via a TTA mechanism because of the insurmountable energy required for the direct PDI\(^{\text{2+}}\) and PDI\(^{\text{3+}}\) recombination to reach a singlet excited PDI. A TTA process is excluded in our case because tenfold increase in the concentration of 1c had no impact on the kinetic data or the quantum yields. The luminescence signal of 1c decays in several nanoseconds in all solvents, similar to endothermic singlet fission observed in tetracene dimers.\(^\text{39} \) Despite the singlet fission being slightly endergonic in PDI solids due to strong PDI–PDI coupling, the reported triplet energy of PDI in a solution is \( E_T = 1.1–1.2 \) eV (ref. 40) (DFT: 1.22 eV, see the ESI†). Considering the \( E_{0-0} = 2.35 \) eV in 1c, the resulting energy change is nearly isoeergic and admixture of a CT character into S\(_1\) state, as revealed recently by Hong et al.,\(^\text{14} \) can lead to a slightly exoergic process in accord with \( \Delta G_{\text{proc}} \). Nevertheless, eqn (4), which is based on a hard spheres model, has been shown to break down in some macrocyclic compounds that contain substituted PDI chromophores\(^\text{18} \) and the actual values of \( \Delta G_{\text{CS}} \) are in fact less negative than the values predicted with eqn (4). Note, however, that the difference in \( \Delta G_{\text{CS}} \) in different solvents matches the experimentally determined difference in \( \Delta G_{\text{proc}} \) remarkably well. Overall, sole thermodynamic considerations are not conclusive in our case.

We then tested the effect of molecular oxygen on the excited state lifetime of 1c by saturating its benzonitrile solution (Table S8†). Indeed, we observed a reduction of \( \tau_{\text{delayed}} \) and \( \phi_{\text{em}} \) from 55.9 to 10.7 ns and from 0.4 to 0.27, respectively. However, \( \tau \) of 3c was affected, too, although to a smaller extent (2.7 times less), which suggests that superoxide species could be generated instead of singlet oxygen.

Finally, we performed transient absorption spectroscopy of 1c and followed the evolution of the excited state processes from a few picoseconds to hundreds of nanoseconds in benzonitrile. Fig. 5 shows the obtained transient absorption spectra. An intermediate with a maximum of absorption at 615 nm and a shoulder at 575 nm, which we assign to S\(_1^\text{st} \), formed (1.50 ns) and decayed (50.9 ns; Fig. S68†) with time constants that matched very well the \( \tau_{\text{prompt}} \) and \( \tau_{\text{delayed}} \), respectively, from the TCSPC measurements. The delayed fluorescence and the recovery of the ground state bleach parallel kinetically the S\(_1^\text{st} \) disappearance and confirm that this intermediate both repopulates the S\(_1 \) state and decays directly to the ground state of 1c, respectively. Our results suggest that no or little of PDI triplets form. The signal of S\(_1^\text{st} \) in toluene is absent. In order to assign the nature of S\(_1^\text{st} \) state, we performed a chemical reduction of 3c with cobaltocene in dry benzonitrile and measured the absorption spectrum (Fig. S69†) of the ensuing radical anion, PDI\(^{-} \). The absorption maxima of PDI\(^{-} \) do not match the absorption band observed in our time-resolved experiments and are located outside our detection window. Since oxidation of 1c or 3c is not reversible, we could not measure the absorption spectrum of the corresponding PDI\(^{-} \). Nevertheless, PDI\(^{-} \) generated from related PDI derivatives\(^\text{13,14} \) possess an absorption that matches the observed spectroscopic signature of the generated transient. Hong et al.,\(^\text{14} \) attributed a similar transient feature at 615 nm to the ME state. We assign the observed absorption of S\(_1^\text{st} \) to PDI\(^{-} \) generated by a CS process because a CT-mediated singlet fission mechanism requires a virtual intermediary CT state, which, in our case, represents a shallow energy trap (Scheme 3; see both the \( \Delta G_{\text{CS}} \) or \( \Delta G_{\text{proc}} \)). Note, however, that we do not fully discard a possibility that the observed intermediate also involves a ME state in an equilibrium. The complex and intriguing photochemical behavior of 1c requires a detailed time-resolved spectroscopic analysis including NIR and IR domains. Such work is currently ongoing in our laboratories and will be communicated in a follow-up report.

![Fig. 5 Transient absorption spectra (temporal resolution: ps – top, ns – bottom) measured at various time delays after 532 nm excitation of 1c in benzonitrile. The break in the spectra (top) is due to scattering of the pump light.](image-url)
suggest that a rapid (pseudo)equilibrium establishes between the
in its structure. Our spectroscopic and electrochemical data
as a consequence of the precise spatial arrangement of the PDI units
charge-separated state. Dashed arrows: not observed.

1c resulted in a gate opening phenomenon during adsorption of N2
useful applications in photocatalysis or solar energy storage.

1c (Scheme 3) is an excited state symmetry-breaking
chemical phenomena, such as excited state symmetry-breaking
a development of new porous materials that incorporate photo-
arrangement of the rylene units in the studied cages promises

Thus, we demonstrate that rylene cages integrate the advan-
tages of both porous and electronic materials, a feature typically
observed in nanoscale materials, such as covalent organic frame-
works, but rare in porous organic cages. The three-dimensional
arrangement of the rylene units in the studied cages promises
a development of new porous materials that incorporate photo-
chemical phenomena, such as excited state symmetry-breaking
charge separation, that, when combined together, may lead to
useful applications in photocatalysis or solar energy storage.

Author contributions

T. Š. conceived the research idea, designed the compounds and
performed all calculations. T. Š., A. C. and H.-H. H. designed the experiments and H.-H. H., T. Š. and R. M. synthesized the compounds. A. P. performed the XRD analysis. K. S. S and A. C. investigated the porosity and analyzed the data. H.-H. H. performed electrochemistry, photochemical steady state and TCSCPC experiments and analyzed the data with T. Š. Transient absorption spectroscopy was performed by A. A., G. C., and E. V. The manuscript was written by T. Š., H.-H. H., and A. C. with contributions from all authors.

Conclusions

We synthesized a series of chiral imine organic cages that incor-
porate three redox-active rylene units in their structures and
explored their textural and optoelectronic properties. Thereby, we
showed that the rylene cages are porous and their optoelectronic
properties can easily be tuned by synthesis. NDI and PMDI cages
1a, b showed a good selectivity for adsorption of CO2 over N2 an
CH4 and the flexible nature of PMDI cage 1b in the solid state
resulted in a gate opening phenomenon during adsorption of N2
and Ar at 77 K. In addition, we discovered that the PDI cage 1c
is the first organic cage that displays a delayed fluorescence,
a consequence of the precise spatial arrangement of the PDI units
in its structure. Our spectroscopic and electrochemical data
suggest that a rapid (pseudo)equilibrium establishes between the
singlet excited state of 1c and the intracage charge-separated state
where two PDI units disproportionate into radical ions. The
delayed fluorescence emanates by re-population of the bright
singlet excited state of 1c when the PDI radical ions recombine.

Thus, we demonstrate that rylene cages integrate the advan-
tages of both porous and electronic materials, a feature typically
observed in nanoscale materials, such as covalent organic frame-
works, but rare in porous organic cages. The three-dimensional
arrangement of the rylene units in the studied cages promises
a development of new porous materials that incorporate photo-
chemical phenomena, such as excited state symmetry-breaking
charge separation, that, when combined together, may lead to
useful applications in photocatalysis or solar energy storage.

Notes and references


15 We abbreviate the all-R enantiomer of 1 as (RRR)-1, because the precursor diamines 2 are synthesized from (1R,2R)-(−)-diaminocyclohexane. Accordingly, the all-S enantiomers are synthesized from (1S,2S)—(+)-diaminocyclohexane (see the ESIF for further details).


37. We observed that the oxidation of both 1c and 3c in CH2Cl2 was irreversible. Therefore, the oxidation potential of related N,N′-dicyclohexylperylene-3,4:9,10-tetracarboxydiimide in CH2Cl2 (1.16 V) was used. Note that the first reduction potential of this compound is nearly identical to that of 1c (Table S2†). See compound “12” in Table 3 in: C. Zhao, Y. Zhang, R. Li, X. Li and J. Jiang, *J. Org. Chem.*, 2007, 72, 2402–2410.

