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Guest Inclusion Modulates Concentration and Persistence of Photogenerated Radicals in Assembled Triphenylamine Macrocycles.

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ABSTRACT: Substituted triphenylamine (TPA) radical cations show great potential as oxidants and as spin containing units in polymer magnets. Their properties can be further tuned by supramolecular assembly. Here, we examine how the properties of photogenerated radical cations, intrinsic to TPA macrocycles, are altered upon their self-assembly into 1D columns. These macrocycles consist of two TPAs and two methylene ureas which drive the assembly into porous organic materials. Advantageously, upon activation the crystals can undergo guest exchange in a single-crystal-to-single-crystal transformation generating a series of isoskeletal host-guest complexes whose properties can be directly compared. Photoinduced electron transfer, initiated using 365 nm LED's, affords radicals at room temperature as observed by EPR spectroscopy. The line shape of the EPR spectra and the quantity of radicals can be modulated by both polarity and heavy atom inclusion of the encapsulated guest. These photogenerated radicals are persistent, with half-lives between 1-7 days and display no degradation upon radical decay. Re-irradiation of the samples can restore the radical concentration back to a similar maximum concentration, a feature that is reproducible over several cycles. EPR simulations of a representative spectrum indicate two species, one containing two N hyperfine interactions and an additional broad signal with no resolvable hyperfine interaction. Intriguingly, TPA analogs without bromine substitution also exhibit similar quantities of photogenerated radicals, suggesting that supramolecular strategies can enable more flexibility in stable TPA radical structures. These studies will help guide the development of new photoactive materials.

INTRODUCTION

Construction of hierarchical materials through supramolecular assembly of small molecules is an expedient method for crafting materials with useful properties.1-4 These properties range from conductivity,⁵ magnetism,⁶ to dichromism.7 In addition, supramolecular assembly can also be used to make porous materials that encapsulate small guests.^{8,9} This leads to materials of use in catalysis,^{10,11} storage,^{12,13} confinement,¹⁴ separation,^{15,16} and sensing.^{17,18} Furthermore, bound guests may alter the chemical and physical properties of the host itself, for example, modulating the rotational speed of host-bound molecular rotors¹⁹ or expanding/contracting the host framework.^{20,21} Here, we investigate how different guests encapsulated within a triphenylamine (TPA) host affect its ability to form radicals in the solid-state upon UV irradiation (Figure 1). The host is robust and exchanges guests via single-crystal-to-singlecrystal (SC-SC) transformations while retaining its original



Figure 1. Self-assembly of TPA macrocycles results in the formation of a columnar assembled host. Activation of this host by heating allows for the introduction of new guests via SC-SC transformations. Each complex generates radicals upon irradiation with 365 nm LEDs, affording EPR spectra with different line shapes and intensities. A comparison of four of these EPR is shown above (benzene, 1,4-dioxanes, DME, and DMF). The insets for each graph show structure of the guest, SC-XRD of the host-guest complex, and the percent of molecules that generate a radical upon UV-irradiation at the maximum radical concentration compared to the total number of molecules in the bulk material.

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framework. This affords a series of isoskeletal host-guest structures whose properties can be directly compared. Upon UV irradiation of the host, long-lived radicals are generated. Encapsulated guests within the host modulate the line shape of their EPR spectra and the concentration of radicals observed during irradiation. Additionally, after decay of the photogenerated radicals, samples can be reirradiated to regenerate the observed radicals without harming or degrading the TPA host. Understanding how guest inclusion affects these radical properties will be useful for designing the next generation of conductive and magnetic materials.

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Organic radicals have many uses, ranging from MRI contrasting agents²² to multifunctional magnetic materials.²³ One class of these radicals are TPA radical cations, which have undergone a single electron oxidation from their neutral state.²⁴ Key to their stability is the presence of *para* substitution on all three phenyl rings of the TPA system, which slows degradation reactions such as benzidine formation.^{25,26} This is seen for Magic Blue, a commercial oneelectron oxidant,^{27,28} as it has bromine substitution on all three *para* sites of the TPA. When stabilized, TPAs find use as high-spin polymers,^{29,30} cathodes in batteries,^{31,32} and as hole-transport layers in solar cells.³³ Typically, these radicals are formed through chemical or electrochemical oxidation pathways,³⁴ but they may also be generated by UVirradiation when an electron acceptor is present.^{35,36}

Our group employs the three-centered urea hydrogen bonding interaction to organize linear and macrocyclic compounds in high fidelity. This affords nanoporous materials that are typically used as nanoreactors for photochemical reactions.37 In addition to forming nanochambers, these structures also exhibit markedly different photophysical properties when compared to their unassembled monomers in solution. For example, assembly of benzophenone containing urea macrocycles and linear analogs display surprisingly stable radical formation upon UVirradiation; this behavior is not observed in solution.³⁸ Similarly, brominated TPA 2a (Figure 2) also shows enhanced stability of photogenerated radicals within its assembled structure, while radical formation in solution results in complete degradation of the TPAs.39 Thus, demonstrating the importance of supramolecular assembly on the overall stability of the photogenerated radicals. Here, we investigate if TPA containing macrocycle system, 1a, also exhibits enhanced photogenerated radical stability upon self-assembly.

TPA **1a** self-assembles to form a porous host that can facilitate guest inclusion and removal via SC-SC crystal transformations.⁴⁰ By irradiating this host we can probe if macrocycle **1a** exhibits similar radical formation as its linear analog counterpart **2a** and if guest inclusion alters the process of radical generation within the host. Thus, the photophysical properties and photogenerated radical formation of this host were investigated. The guests in these studies were selected to cover a range of polarities as well as heavy atom inclusion. Control compounds **1**, **2**, and **3-4** were prepared to elucidate the structure of the photogenerated radicals and to identify the features of these assembled TPA systems that allow for stable radical formation. Our goal is to understand the effects different guests have on radical formation and to determine what characteristics are necessary for TPA-containing compounds to exhibit these properties.

RESULTS AND DISCUSSION

Macrocycles (1 and 1a) and linear analogs (2 and 2a) were synthesized in five steps following established methods (Scheme S1).^{39,40} For macrocycle 1, its dibromide and protected macrocycle precursor were structurally characterized (see SI). Control compounds 3 and 3a were purchased from commercial suppliers, while control 4 was synthesized in two steps using a Vilsmeier–Haack reaction to yield the aldehyde,⁴¹ followed by a reductive alkylation of urea to give the desired product.⁴² Host-guest crystals of 1 and 1a were obtained from vapor diffusion of either water or 1,2-dimethoxyethane (DME), respectively, into DMSO solutions. Solvent free crystals for 2-4 were grown via slow evaporation of acetonitrile (2 and 3a), ethyl acetate (2a), or ethanol (3); or by vapor diffusion of water into a DMF solution (4).



Figure 2. Comparison of TPA structures investigated. Macrocycles 1 and 1a, linear analogs 2 and 2a, and control compounds 3, 3a, and 4 are shown.

For TPA 1, the X-ray structure revealed the desired macrocycle in the space group P_{2_1}/n of the monoclinic system. The macrocycles were found in the syn conformation organized into tubular columns encapsulating disordered DMSO in a 1:1 host-guest ratio. The syn conformation was surprising as previous bis-urea macrocycles crystallize in the anti-conformation, where the urea groups in a single macrocycle are oppositely aligned to minimize dipole interactions.³⁷ Despite this, the macrocycles still organize into columns through the characteristic three-centered urea hydrogen bond (*d*(N···O) = 3.090(5), 3.078(5), 3.147(5), and 3.063(5) Å). Additional stabilization occurs through intracolumnar edge-to-face π -stacking of the TPA groups (Figure S22). This stacking affords individual nanotubes with a pore aperture of 6.4×4.3 Å after accounting for the van der Waals (vdW) radii of the participating atoms (Figure 3A, top). The resulting nanotubes pack together to form robust hexagonal arrays as seen in Figure S16.

For comparison, the brominated macrocycle, **1a**, crystallizes as colorless needles in the space group $P_{2_1/c}$ of the monoclinic system.⁴⁰ This macrocycle adopts the typical *anti* conformation and organizes into columnar tubes. The channels display an interior cross-section diameter of 6.5 × 4.3 Å and contain encapsulated, disordered DME (Figure 3B, right) in a host-guest ratio of 2:1. The tubes form along the crystallographic *b* axis and are held together via

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Figure 3. Comparison of TPA hosts 1.DMSO and 1a.DME. (A) Comparison of cross-sectional areas with 1 on top and 1a on bottom (subtracting vdW radii). (B) Comparison of columnar structures with guests included with 1.DMSO on the left and 1a.DME. Disorder in the guests has been omitted for clarity.

hydrogen bonds between the ureas $(d(N \cdots O) = 2.848(4))$ and 2.929(4) Å) and π -stacking between neighboring TPAs. Individual columns are held together with π - π and halogen- π stacking interactions forming a hexagonal array similar to 1-DMSO.

To generate different host-guest complexes of host 1a, crystals of 1a·DME were activated and loaded with new guests via SC-SC transformations.⁴⁰ Crystals of 1a·DME were activated by heating under vacuum at 90 °C for 2.5 h to remove the DME. Next, a series of host-guest complexes (Figure 4) were prepared by immersing the activated crystals in a guest solution for 24 h. Afterwards, the crystals were filtered and air dried affording the new host-guest complex. The activated host and benzene derivative loaded hosts of 1a have been previously characterized via SC-XRD and are all isoskeletal in regard to the macrocycle framework of 1·DME. New to this work, DMF and 1,4-dioxanes were also loaded into the nanotubes. Again, the host framework remained isoskeletal.

In the benzene derivative loaded hosts of **1a**, (Figure 4), the guests were arranged in a planar tape-like manner inside the channels and were modeled on two crystallographic independent sites.⁴⁰ These sites were located near inversion centers giving four possible sites for guest location. Each of these sites had similar occupancy giving an approximate host-guest ratio of 1:0.5. The 1,4-dioxane and DMF-loaded **1a** complexes exhibited a very similar guest disorder, although 1,4-dioxane was modeled on three independent crystallographic sites instead of two. Overall, the 1,4-dioxanes and DMF guests exhibited host-guest ratios of 1:0.58(2) and 1:0.65(1), respectively. These loading ratios were higher compared to all the other modeled complexes, likely a result of the smaller size of these guests.

For comparison to the macrocycles, linear analog 2 crystallized in the orthorhombic system in the centrosymmetric space group *Pbcn*. In this structure, both TPA groups extend to either side of a disordered methylene urea tether in a linear *trans-trans* arrangement (Figure 5). The disorder in the urea tether is oriented either up (50%) or down (50%) relative to the *c* axis, forming three-centered urea hydrogen bonded chains ($d(N \cdots O) = 2.749(8)$ and 2.716(8)Å). The TPA groups, which are not disordered, organize in a cruciform pattern in relation to the urea chain with edge-



Figure 4. Guest inclusion complexes of 1a with their host-guest ratios. (A) Heating of 1a DME results in an activated host. (B) Guests can then be added upon submersion of the activated crystals into a liquid of the new desired guest, resulting in SC-SC transformation to afford a new host-guest complex. The DME complex, activated host, and four benzene derivative guest complexes have been previously reported,⁴⁰ while the DMF and 1,4-dioxane structures are new to these studies.

to-face π -stacking from the TPAs holding alternating chains together (Figure S₂₃).



Figure 5. Comparison of triphenylamine linear analogs **2** (left) and **2a** (right). (A) Three-center urea hydrogen bonding interactions stack the triphenyl amine groups on top of one another forming urea tape motifs. (B) Top-down view of the urea tapes showing either a cruciform pattern (left) or X-shaped pattern (right).

The brominated derivative **2a** was similarly organized in the orthorhombic system in the *Pccn* space group.³⁹ TPA **2a** was also found in a linear *trans-trans* arrangement with both TPA groups extended out on either side of the methylene urea tether (Figure 5). The TPA units show minor disorder in this structure (5% to 9% depending on the chosen crystal) resulting from an opposite TPA rotation relative to the urea group. Overall, the urea groups still organize **2a** into chains along the crystallo-graphic *c* axis (*d*(N···O) = 2.823(3) and 2.70(2) Å), resulting in an X-shape pattern in projection along the chain direction instead of the cruciform pattern observed for TPA **2**.

Triphenylamines (3 and 3a) and urea derivative 4 were also crystallized. Together with the linear analogs and macrocycle 1, this provides a series of control compounds

for photophysical studies of macrocycle **1a**. The structure of TPA 3 has been previously reported (CCDC# 1319035), and it crystallized in the monoclinic system in the Bb space group with multiple edge-to-face π -stacking interactions driving the assembly.43 For TPA 3a, two different polymorphs were found, crystallizing either as colorless needles (triclinic system, P-1 (No.2) space group) or as colorless blocks (monoclinic system, P_{2_1}/c space group). The packing in both polymorphs was primarily driven through edge-to-face π stacking interactions (Figures S24 and S25); however, the bromines stacked much closer to each other in the monoclinic polymorph (4.473 Å vs 6.230 Å). According to powder X-ray diffraction results, the bulk sample most similarly matched the monoclinic polymorph (Figure S30). Lastly, TPA 4 crystallized in the monoclinic space group P_{2_1}/c as colorless flakes. Assembly was organized through the three-centered urea hydrogen bond forming twisted chains along the crystallographic c axis similar to **2a** $(d(N \cdots O) = 3.069(3)$ and 3.028(2) Å) with additional stabilization coming via edge-to-face π stacking interactions (Figure S₂₆).

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To probe how structure, self-assembly, and guest encapsulation effects the photophysics of macrocycle 1a, the absorption, emission, and photoluminescence lifetimes for solution and solid-state samples were measured. Table 1 compares the photophysics of macrocycle 1a and linear analog 2a as 10 µM solutions in nitrogen purged DMSO to the assembled crystals of 1-2a and some guest inclusion complexes of host 1a. In solution, macrocycle 1a exhibits only one band in its absorption spectra with a λ_{max} at 303 nm and molar absorptivity of $\sim 5 \times 10^4$ M⁻¹ cm⁻¹ which is similar to its linear analog counterpart 2a under comparable conditions.³⁹ In the emission spectra, macrocycle 1a shows two bands, with a smaller one at 378 nm and the larger at 450 nm, also quite similar to linear analog 2a. The photoluminescence lifetime of macrocycle 1a was guite short and approximately half of what was observed for linear analog 2a (2.3 ns versus 4.1 ns).

In the solid-state, activated host **1a** showed a 60 nm redshift of the absorption maxima versus dissolution in DMSO going from 303 to 366 nm (Figure S38). The formation of an additional broad absorption band at ~400 nm was also observed. The shift in absorption is more typical for J- aggregation in planar dyes.⁴⁴ However, Yang et al. observed such shifts in a crystalline styrene derivatized TPAs⁴⁵ and we also observed a similar shift for the related linear analog 2a.³⁹ Similar absorption spectra were also observed for 1a·DME, 1a·C₆H₆, and 1a·DMF. These host-guest complexes were chosen because of their polarity differences since polarity played a large role in determining the photophysical properties of linear analog 2a in solution. Interestingly, the non-brominated TPAs of macrocycle 1 and linear analog 2 also exhibited a red-shift in absorption, although their broad band at ~400 nm is comparatively more intense.

Assembly had less influence on the emission spectra and photoluminescent lifetimes for macrocycle 1a. Indeed, activated host 1a and its complexes (1a·DME, 1a·C₆H₆, and 1a·DMF) exhibited similar λ_{max} of emissions at ~460 nm upon excitation at the λ_{max} of absorption with similar lifetimes of ~1.2 ns. For comparison, activated 1, 2, and 2a³⁹ show similar behavior with the non-halogen containing compounds exhibiting marginally longer lifetimes (1.5 ns) likely due to the lack of a heavy atom. Our hypothesis is that these shortened lifetimes are a result of non-radiative pathways which may include radical formation.

Previously, we reported that UV-irradiation of linear analog 2a generated radicals, which were unstable in solution resulting in degradation of the material.³⁹ Intriguingly, the radicals were found to be stable and persistent when generated within the assembled structures. Thus, we irradiated the activated host of 1a to see if similar radicals would be observed. For this, freshly activated 1a was sealed under Argon and was examined by X-band EPR spectroscopy pre and post irradiation. For UV-irradiation, 365 nm LEDs were employed instead of the medium pressure Hg lamp used previously.^{38,39} The 365 nm LEDs are close to the λ_{max} of absorbance for these materials and show significant reduction in the background signal (see SI). Figure 6A compares the EPR signal of 1a after 4 h of irradiation versus the pre-UV sample. After exhibiting very little signal pre irradiation, the EPR signal exhibits a broad, axial powder pattern shape with a *g*-value of 2.008 post irradiation.

Next, we measured the EPR signal of activated **1a** (9.8 mg) under increasing irradiation time (1 to 24 h) to see if more radicals would be generated with longer irradiation times. To monitor the formation of radicals, we plotted the

| Compound | $\lambda_{abs} (\mathbf{nm})^a$ | $\epsilon (\times 10^4 M^{-1} cm^{-1})$ | $\lambda_{ems} (nm)^b$ | $	au_{}(ns)^c$ |
|--|---------------------------------|---|------------------------|------------------|
| 1 | 369, 414 | | 478 | 1.6 |
| 10 μM 1a in DMSO | 303 | 4.65 | 378, 450* | 2.3 |
| 1a | 366 | | 465 | 1.1 |
| 1a DME | 377 | | 456 | 1.4 |
| $1 \mathbf{a} \cdot \mathbf{C}_6 \mathbf{H}_6$ | 370 | | 455 | 1.2 |
| 1a DMF | 372 | | 456 | 1.3 |
| 2 | 366 | | 487 | 1.5 |
| 10 μM 2a in DMSO | 302 ^d | 5.41 ^d | 369, 452* ^d | 4.1 ^d |
| 2a | 358 ^d | | 447 ^d | 1.0 ^d |

Table 1. Measured photophysical properties for compounds 1, 1a, 2, and 2a with different conditions.

^a Peak position at largest absorption band. ^b Peak positions at largest emission bands in nm (largest denoted with * if applicable, excited at $\lambda_{abs.}$). ^b Average lifetime of the most intense emission peak. ^d Values taken from reference.³⁹

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Figure 6. EPR studies for activated **1a**. (A) EPR signal pre and post UV irradiation. (B) Double integration over time of UV irradiation. (C) Dark decay spectra for activated **1a** after it was irradiated to its maximum radical concentration. (D) Double integration versus time after irradiation.

double integration of the EPR spectra over time. To estimate the number of radicals generated, the double integration of the EPR spectra were compared to a calibration of Magic Blue standard solutions in dichloromethane (Figure S68). A comparison of these can give an approximate concentration of the number of radicals generated in the solid-state. As seen in Figure 6D, the concentration of radicals grows with increasing irradiation time until it plateaus around 20 h. At this point, ~ 0.69% of the molecules generated a radical (or ~ 1 in 150 molecules) which estimates to the same number of radicals seen in 100 μ L of a 0.83 mM solution of Magic Blue.

Next, seven host-guest complexes of 1a were systemati-29 cally investigated to quantify the maximum amount of rad-30 ical they could generate upon irradiation. These complexes 31 were chosen as to vary the polarity and heavy atom substi-32 tution of the guests to see if they had any effects on radical 33 formation. As seen in Figures S61-67, most of these com-34 plexes reached their maximum EPR signals after ~ 20-24 h, 35 apart from $1a \cdot C_6H_5F$ and $1a \cdot C_6H_5Cl$ which reached a maxi-36 mum after 12 h. Interestingly, the presence of encapsulated 37 guests altered both the line shape of the signal as well as 38 the quantity of radicals formed as seen in Figures 1 and 7; 39 and Table 2, respectively. This was guite surprising since 40 guest encapsulation had little effect on the absorption, 41 emission and lifetimes of host 1a. For the line shapes, the 42 least polar and least heavy atom substituted complex, 43 $\mathbf{1a} \cdot \mathbf{C}_6 \mathbf{H}_6$, showed the line shape most similar to the empty 44 structure, activated 1a, while the more polar, heavy atom 45 complexes of $1a \cdot DMF$ and $1a \cdot C_6H_5Br$ showed a narrowing 46 of the line shape. Similarly, the least polar and least heavy 47 atom substituted complex, $1a \cdot C_6 H_6$, generated the most 48 radicals (0.78%) while the more polar, heavy atom substi-49 tuted complexes of 1a·DMF and 1a·C₆H₅Br exhibited the 50 least number of radicals (0.15% and 0.23%, respectively). In 51 fact, trends were observed along these lines with polarity 52 $(\mathbf{1a} \cdot C_6 H_6 > \mathbf{1a} \cdot \mathbf{1}, 4 \cdot \text{dioxanes} > \mathbf{1a} \cdot \text{DME} > \mathbf{1a} \cdot \text{DMF})$ and heavy 53 atom incorporation $(\mathbf{1a} \cdot C_6 H_6 > \mathbf{1a} \cdot C_6 H_5 F > \mathbf{1a} \cdot C_6 H_5 Cl >$ 54 $1a \cdot C_6 H_5 Br$) clearly affecting the amount of radical ob-55 served. Intriguingly, encapsulation of benzene within host 56 1a afforded an even higher radical concentration than acti-57 vated 1a. This may be due to a stabilization of the framework, or because the filled channel slows down oxygen quenching processes.



Figure 7. EPR studies for guest inclusion complexes of 1a. EPR signal pre and post UV irradiation is given for each complex. Additionally, the *g*-values are given.

| Table 2. Approximateirradiation from 365 nm | number of LEDs. | radicals | generated | during | UV- |
|--|-----------------|----------|-----------|--------|-----|
| | | | | | |

| Compound | 4 Hours | Max |
|--------------------------------|-------------------------|--------|
| 1 | 0.69% | |
| 1a | 0.42% | 0.69% |
| 1a ·DME | 0.20% | 0.28% |
| $1a \cdot C_6H_6$ | 0.55%ª | 0.85%ª |
| 1a ·C ₆ H₅F | 0.33% | 0.45% |
| 1a·C ₆ H₅Cl | 0.19% | 0.24% |
| 1a ·C ₆ H₅Br | 0.13% | 0.23% |
| 1a ·1,4-dioxanes | 0.24% | 0.38% |
| 1a·DMF | 0.08% | 0.15% |
| 2 | 0.16% | |
| 2a | 0.16% | |
| 3 | ~ 0% | |
| 3a | Very Small ^b | |
| 4 | Very Small ^b | |

^a Average of four trials. A standard deviation of 0.06% was found for these trials. This is considered to be the error in all the measurements taken. ^b Concentration below values of calibration curve given in Figure S68.

To further estimate the error of these measurements, we repeated the $\mathbf{1a}$ -C₆H₆ experiment three more times, by irradiating the sample until radical formation plateaued (Figure S61). On average 0.85% of the molecules generated a radical at maximum concentration (or 1 in 120 molecules) with a standard deviation of 0.06% which is considered to be the error on all the other measurements. Overall, this demonstrates the reproducibility of radical concentrations between samples.

Next, the persistence of the photogenerated radicals were examined with dark decay studies. For this, samples which were irradiated to their maximum concentration, were stored in the dark at room temperature. Then EPR spectra were taken periodically afterwards to assess the stabilities of the radicals. Figures 6C and 6D show the EPR signal and the double integration of the EPR signal, respectively, over time for the activated **1a** host over three weeks.

Figure 6D shows that the number of radicals decays to about 20% of the maximum concentration after one week, with an estimated half-life of ~ 24 h. The remaining radical species display more stability, with their concentration remaining somewhat constant up to three weeks later. These results in combination with the different line shapes shown in the latter spectra (Figure 6C), suggest that at least two types of radical decay processes are occurring. Simulations of the EPR spectra (see below) also support this suggestion.

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10 For the host-guest complexes, dark decay studies were performed on complexes $1a \cdot C_6 H_6$, $1a \cdot DME$ and $1a \cdot DMF$ as 12 these guests afforded the greatest difference in radical con-13 centrations (Table 2). Similar behavior and half-lives were 14 observed for $1a \cdot C_6 H_6$ and $1a \cdot DMF$ crystals when compared to activated 1a (Figures S61 and S63). A longer half-life of ~ 15 1 week was estimated for the 1a. DME complex (Figure S62). 16 Additionally, the radical concentration only dipped to about 40% of its maximum after 3 weeks instead of 20% 18 which was observed for all the other cases for host 1a. This 19 enhanced stability may be a result of minimal processing, 20 as complex 1a. DME is formed during the initial crystallization conditions for macrocycle 1a. Activated 1a is prepared 22 by heating complex 1a.DME to remove the DME guest. 23 Complexes $1a \cdot C_6 H_6$ and $1a \cdot DMF$ are formed by soaking ac-24 tivated 1a crystals in neat C_6H_6 or DMF. The extra steps in 25 crystal processing may explain why these three materials 26 exhibit a shorter radical lifetime versus complex 1a.DME during the dark decay of the radical signal. In fact, linear 28 analog 2a which also had minimal processing, displayed a 29 similar half-life (1 week), and decayed to only $\sim 40\%$ of its 30 initial signal similar to complex 1a. DME.39 Therefore, there is significant similarity between freshly crystallized sam-32 ples. Overall, the line shapes of the EPR spectra for each 33 case involving macrocycle 1a decayed to very similar signal 34 levels, suggesting that the longer-lived radical species 35 among these samples is similar.

36 Usually with chemical or electrochemical radical gener-37 ation methods, the sample must be resynthesized once the 38 TPA radicals have decayed due to degradation. However, 39 no degradation was detected by NMR for linear analog 2a 40 after radical generation.³⁹ Moreover, after radical decay, re-41 exposure of linear analog 2a to UV-light led to regeneration 42 of the radical species. This led us to test four samples of 43 host 1a (activated 1a, 1a·DME, $1a \cdot C_6H_6$, $1a \cdot DMF$) to deter-44 mine if similar stable and regenerable radicals would be 45 observed. For these experiments, each sample (5-10 mg) 46 was irradiated to its maximum concentration, its EPR spec-47 trum measured, followed by storage in the dark for two 48 days. EPR signals were recorded at t = 8, 24, and 48 h. Then 49 the samples were re-irradiated (12 - 14 h) so the cycle could 50 be repeated. Figure 8 plots the area of the EPR signal versus 51 time over four cycles of this photo-regeneration process for 52 each sample. Remarkably, in all four cases, the radical signal could be fully restored in both intensity and line shape 53 (Figures S60-S63). For complex $1a \cdot C_6H_6$, the maximum rad-54 ical concentration slightly increased over each cycle. This 55 unexpected result may be a consequence of some charge 56 equilibria during radical decay, allowing for more charge 57

to be introduced during later irradiation, since this is suspected to be a charge separation-based process.³⁹ Overall, in each case radicals could be formed, decay, and then formed again over multiple 2-day cycles, in a reproducible manner.



Figure 8. Regeneration of radical signals for activated 1a, 1a C₆H₆, 1a.DME, and 1a.DMF. After initial irradiation to maximum concentration, each sample was allowed to decay for two days. Then they were re-irradiated overnight to restore radical signal.

After seeing that the radicals could be repeatably lost and regenerated, we wanted to monitor if the host material could survive this process similar to linear analog 2a.³⁹ For this, each sample used from the regeneration studies (activated 1a, 1a·DME, 1a·C₆H₆, 1a·DMF) were dissolved in DMSO- d_6 and their ¹H NMR recorded and compared to a freshly synthesized sample of 1a. As seen in Figures S69-S72, no degradation was observed for any of the samples. Comparing these spectra, the only difference is the presence of guests in the NMR spectra (as is the case with benzene). These studies suggest that radical formation of host 1a is reversible and does not lead to the degradation of the material as a whole.

Next, we compared the EPR spectra for control compounds 1 and 2-4 before and after irradiation (4 h, 365 nm LEDs) to investigate the chemical structure that contributes to radical formation (Figure 9 and Table 2). The first of these, TPA 3, which has no substitution on the TPA group, displayed no significant radical formation after irradiation, suggesting that at least some substitution on the TPA moiety is needed for radical formation in the solidstate. The mono-brominated equivalent of TPA 3, compound 3a, showed a very small signal after irradiation. This signal was so small that it was below the detection limits of our calibration curve to quantify the radical concentration. This suggests that the signal from TPA 3a does not arise from the same process as macrocycle 1a as many more radicals were produced for macrocycle 1a. The radicals generated from TPA **3a** may just be the result of photolysis of the C-Br, bond which can be expected for halogenated aromatics.⁴⁶ Control 4, which has one methylene urea connected to the TPA group, also exhibited a very small signal similar to the singly brominated TPA of 3a suggesting that it may also be susceptible to a small amount of photolysis.

Given these controls, we suspected that closely organizing two TPA units in a linear or macrocyclic system is

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important for generating significant radical concentrations in the solid-state. Therefore, we tested the non-brominated analogs of macrocycle 1a and linear analog 2a to see if they afforded significant amounts of radical. Indeed, nonbrominated linear analog 2 forms a similar number of radicals as its brominated counterpart, 2a, after 4 h of irradiation (both \sim 0.16%). Surprisingly, the non-brominated macrocycle 1 exhibited the highest efficiency of radical generation after four hours of irradiation (0.69% for the non-brominated macrocycle 1 versus 0.42% for the brominated macrocycle of 1a) and showed more hyperfine interactions than its linear counterpart, 2. Considering that macrocycle 1a also had more hyperfine splitting than its linear analog counterpart 2a, this suggests that the additional tether between the TPAs (macrocycles having two and linear analogs having one) increases the hyperfine splitting in the EPR spectra.



Figure 9. EPR signals pre and post irradiation for control samples 1, 2, 2a, 3, 3a, and 4. Each sample was irradiated for four hours before the post-irradiation EPR spectra were taken.

To investigate how UV-induced radical formation affected the TPA materials and to probe insight into a possible mechanism of radical formation, both linear analog 2a and the activated host of 1a were further investigated by Cross-Polarized Magic Angle Spinning (CP-MAS) ¹³C NMR. Overlays of the NMR spectra of the pre- and post-irradiated solids are shown in Figure S73. While the methylene carbon resonances of the urea linker (ca. 43 ppm) were minimally affected, the overlays reveal significant UVinduced broadening of the aromatic and carbonyl ¹³C lines, particularly for linear analog 2a. Thus, the proton spin-lattice relaxation times at different sites in crystals of the UVirradiated linear analog 2a were probed by application of the inversion-recovery pulse sequence to the protons prior to cross-polarization and detection on ¹³C (Figure S74). The longest spin relaxation times were observed for protons attached to the urea linker carbons, consistent with the minimal line-broadening observed at these sites. In contrast,

the T_1 relaxation time of the protons in the vicinity of the carbonyl carbon were among the shortest in the sample, where the recovery null occurs at approximately 3.5 s. The proton T_1 of the protons on the aromatic rings varied and was shortest for broad resonance at ~120 ppm and increased with increasing chemical de-shielding, consistent with the observed variations in the line broadening. The CP-MAS NMR results suggest localization of unpaired electron density in the BrNPh₃ moiety. Significant line broadening on the carbonyl carbon but not the methylene carbon suggests radical formation impacts the urea network more strongly than the methylene bridge. To probe if the structure of the radicals changes with time, the stability of the UV-induced radicals were monitored over the course of 16 h by acquiring a series of ¹³C CP-MAS spectra every 53 minutes. As seen in the overlay of these spectra in Figure S75, the spectra are all identical (within the noise), demonstrating the stability of the photoinduced radicals on the timescale of this experiment.

To gain more insight into structure of the photogenerated radicals we next investigated the more soluble TPAs 2-4 via electrochemical methods. Prior electrochemical studies with linear analog 2a demonstrated oxidation at 1.0 V versus a saturated calomel electrode (SCE) as a 1 mM solution in dichloromethane. This resulted in a dication with both TPA groups containing a radical cation.³⁹ Bulk electrolysis at this potential exhibited a very similar EPR spectrum to the photogenerated radicals of linear analog 2a in the solid-state indicating that a similar radical species (radical cation) was present in both samples.

For this study, a cathodic investigation of TPA and its related derivatives were investigated with cyclic voltammetry. Voltammograms of TPAs 2-4, Figures S76-S80, all exhibit irreversible reductions occurring between -1.2 and -1.5 V versus SCE as 1 mM dichloromethane solutions. Reduction of TPA **3** occurred with an $E_{p,c} = -1.28$ V under the standard experimental conditions. Reduction of the brominated TPA, 3a, occurred at a less negative potential of $E_{p,c}$ = -1.18 V. This shift can be attributed to the electron withdrawing Br moiety on TPA 3a. In addition, reduction of methylene urea substituted TPA 4 occurred with a negative potential shift relative to TPA 3 likely due to the electron donating behavior of the methylene urea substituent on the TPA core. These redox trends are consistent with previously reported redox behavior for related TPA derivatives.⁴⁷ Furthermore, linear analogs 2 and 2a exhibit two closely spaced 1e⁻ reductions. These reductions are attributed to reduction of the individual TPA units tethered by the urea linkers and illustrates an ability to generate closely spaced radicals.

Using the EPR, NMR, and electrochemical data, we next set out to simulate the EPR spectra of the UV-irradiated activated **1a**. Figure 10 shows our best effort to simulate the EPR spectrum with the most fine structure. The fact that two independent radicals are needed to get this reasonable fit, with all lines accounted for, supports that two radical decay processes may be at play. The discrepancies in intensity on the high field side of the spectrum are almost certainly due to anisotropy in this solid-state spectrum. Furthermore, the presence of a signal carrier with two N hyperfine interactions and one without strongly supports the suggestion above that more than one redox pathway is available to these structures and that both mono-cations and di-cations may be present. Future isotopic substitutions and *in situ* electrochemical EPR experiments are planned in order to explore this further.



Figure 10. Experimental steady–state X-band EPR spectrum (solid black line) of activated host **1a** post UV-irradiation, overlaid onto a best fit simulation (dashed red line) using EasySpin.⁴⁸ The simulation was performed using parameters for two independent radicals. The first has two nitrogen hyperfine interactions with g = 2.0049, $a_N = 39$ Gauss for two equivalent nitrogens, line width (peak to peak) 5 Gauss, and a relative weighting of 0.1. The second radical has g = 2.0087, contains no hyperfine interactions, line width = 20 G, and a relative weighting of 1.1.

Overall, UV-irradiation of self-assembled methylene urea tethered TPA macrocycles gives rise to persistent organic radicals. Guests loaded within the TPA hosts can modulate the concentration of radicals generated with concentrations ranging from 0.15-0.85% of the molecules generating a radical at maximum concentration. These radicals display a half-life of about 24 hours, persist an upwards of 3 weeks, and can be regenerated with additional UV-irradiation to their original maximum concentration without causing degradation to the TPA host. Future work with these TPA hosts could include investigating how different electron accepting guests affect the radical formation of the TPA host and if it leads to any new conductive properties of the material.

CONCLUSIONS

In summary, several TPA derivatives were synthesized and were organized in the solid-state via crystalline assemblies. One of these derivatives, brominated macrocycle 1a, organizes into robust columnar needles and displays 1D porosity through small nanochannels. Inside these channels, small guests can be exchanged via SC-SC transformations without changing the host framework. This creates a series of isoskeletal complexes whose properties can be directly compared. We have monitored how the photophysics and photo-induced radical formation change with the inclusion of different guest molecules.

Although the absorption, emission, and photoluminescent lifetime properties of each complex were somewhat similar, the amount of photogenerated radicals produced by each complex varied considerably. It was found that an increase in polarity or heavy atom substitution decreases the number of radicals observed. This is highlighted in the

complexes of $\mathbf{1a} \cdot C_6 H_6$, $\mathbf{1a} \cdot DMF$, and $\mathbf{1a} \cdot C_6 H_5 Br$, with the first of these displaying the most radical formation after 24 h of irradiation with 0.78% of the molecules generating a radical. The latter two complexes are more polar or contain heavy atoms and show less radical formation after a similar amount of UV-irradiation, 0.15% and 0.23%, respectively. The increase in radical formation by supramolecular encapsulation of less polar guests was surprising and differs from what is predicted in covalent radical systems that are substituted with both electron donating and electron withdrawing groups.49,50 In such push-pull radicals, the captodative effect predicts that the radicals are more stable in polar solvents.⁵¹ However, such effects appear to vary depending on the structure of the radicals. For example, alkoxy cyanomethyl radicals and cyclohexadienyl radicals showed no solvent effect.52,53 Our observations, coupled with the persistent and regenerable nature of radicals in self-assembled TPA materials will help guide the development of new photoactive materials in which the properties can be tuned simply via guest exchange. Thus, future work will focus on the mechanism of how the encapsulated guest and framework affects radical formation and lifetime.

Overall, the complexes reported here show similar radical half-lives of 24 hours and persist up to 3 weeks. Intriguingly, reirradiation of these materials with more UVlight can regenerate radical quantities to similar amounts to their pre-radical decays. In fact, this radical formation/decay process can continue over several cycles with reproducible results and occurs without degradation of the host material. The key to forming these robust materials with regenerative radical properties is connecting two TPAs together through a methylene urea bridge. Although UV-irradiation of simple bromine or methylene urea substituted TPAs resulted in a small amount of radical signal, significant amounts of photogenerated radicals were not observed until the two TPAs were connected. Currently, we are planning Q-band EPR, ENDOR, ESEEM, and SQUID experiments to try and pinpoint the mechanism of radical formation upon UV-irradiation for these materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at http://pubs.acs.org.

Synthetic procedures, product characterization, Xray, photophysical characterization, NMR, EPR, and CV spectra X-ray data for dibromide 1 X-ray data for protected 1.CHCl₃ X-ray data for protected 1.MeOH X-ray data for 1.DMSO X-ray data for 1a.DMF X-ray data for 1a.1,4-dioxanes X-ray data for 2 X-ray data for monoclinic 3a X-ray data for triclinic 3a X-ray data for 4

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Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

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11 Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

SC-SC, single-crystal-to-single-crystal; TPA, triphenylamine;
SCE, saturated calomel electrode; LED, light emitting diode;
DME, 1,2-dimethoxyethane; DMF, *N*,*N*-dimethylformamide;
SC-XRD, single crystal x-ray diffraction; MRI, magnetic resonance imaging, DMSO, dimethylsulfoxide; SCE, saturated calomel electrode; EPR, electron paramagnetic resonance; MAS,
magic angle spinning; NMR, nuclear magnetic resonance;
ENDOR, electron nuclear double resonance; ESEEM, electron spin echo envelope modulation; C₆H₆, benzene; C₆H₆F, fluorobenzene; C₆H₆Cl, chlorobenzene; C₆H₆Br, bromobenzene; vdW, van der Waals.

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