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Nanometer-Sized Reactor—A Porphyrin-Based Model System for Anion Species

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Abstract: Although many cagelike molecules can create a catalytic environment for promoting chemical reactions, the construction of receptors that can host anionic species and sensitize their reaction is novel. Here we report the photochemically induced dimerization of the anion radicals of TCNQ (7,7,8,8-tetracyano-*para*-quinodimethane) in organic solvent under aerobic conditions when they are encapsulated inside a cationic photoactive receptor. There is clear evidence for a rate increase of over two orders of magnitude, photosensitization of the host, and demonstrated turnover of the catalyst.

Keywords: anions · host–guest systems · photosensitization · porphyrins · reactors

Introduction

Developing synthetic host systems that are capable of binding to specifically targeted substrates and then mimicking the various chemical processes in nature have long been significant goals in chemistry.[1] Encapsulation within the inner space[2] of a molecular container can accelerate a reaction,[3] alter the course of reactions in limited quarters,[4] perturb equilibria,[5] contort conformations,[6] and either stabilize reactive reagents[7] or reaction intermediates.[8,9] Intermolecular chemical reactions of two or more substrates encapsulated in a molecular cage can be greatly accelerated and potentially controlled due to the dramatically increased effective molarity and the strictly regulated orientation of the substrates inside the cavity.[3] Such systems[3] artificially mimic the ability of enzymes to manipulate reaction energetics and chemo-, regio-, and/or stereospecificities. Anions have a lower charge to radius ratio, a wide range of geometries, and they are pH sensitive, so the construction of receptors that can encapsulate anionic species and sensitize their reaction is challenging and there is no report until now.

One place to begin the design of synthetic reactors is to combine recognized catalytic moieties with known binding motifs into a single receptor (Figure 1). In this capacity, porphyrins have remarkable photochemical, electrochemical, and catalytic properties that have helped attract attention to their use as reaction centers.[10] 1,2,3-Triazoles are new motifs that can participate in multiple noncovalent interactions, such as anion recognition[11] within flexible[12] and shape-persistent triazolophanes,[13] and in foldamers,[14] and they can help facilitate self-assembly.[15] Herein, we first present the versatile preparation of a nanometer-sized macrocycle based on a photoactive porphyrin moiety and on cationic triazolium and pyridinium units by taking advantage of the Cu^{I}-catalyzed "click chemistry"[16] between azides and acetylenes. Secondly, the anion-binding properties of this cationic macrocyclic host are verified and then employed together with the photochemical porphyrin to establish the use of this macrocycle as a reactor for the dimerization of 7,7,8,8-tetracyano-*para*-quinodimethane (TCNQ) radical anions.

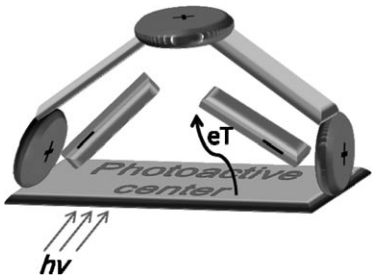

Figure 1. Design strategy of a photoactive nanoreactor.

The dimerization of $[TCNQ]^{-\cdot}$ radicals was selected as a model reaction on account of the anionic charge of the reactants and the existing knowledge of its dimerization (Figure 1). The formation of $[TCNQ]_2^{2-}$ dimers has been ex-

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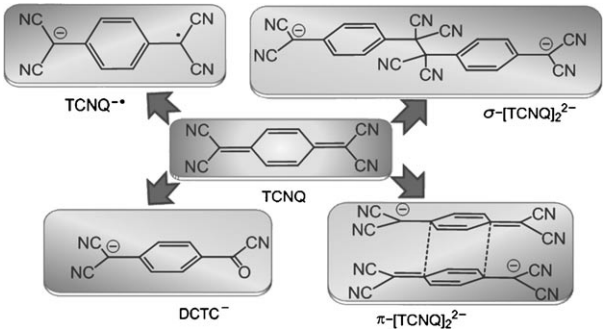
perimentally reported[17] in both solids and aqueous solution.[17b,d] The dimers are linked by either σ or π bonds (Scheme 1). The π-$[TCNQ]_2^{2-}$ dianion dimers have long, multicenter intradimer C–C bonding,[17c,d,f] whereas the σ-



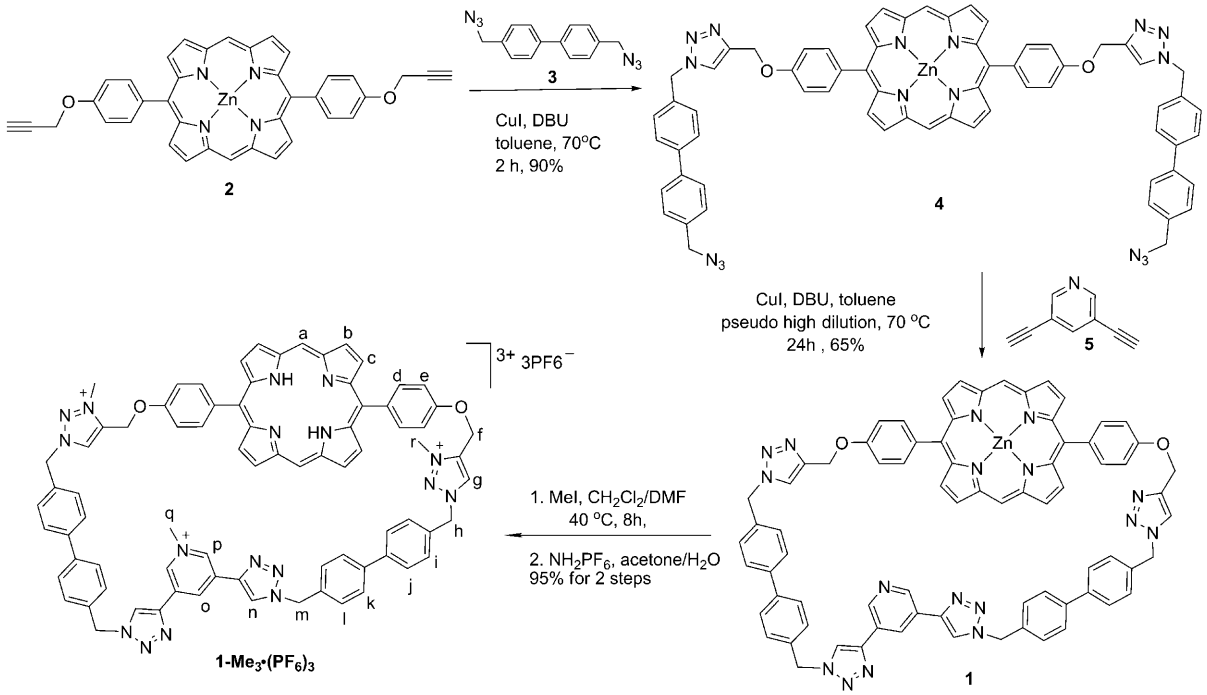
Scheme 1. Different forms of TCNQ and its possible reaction products. The σ- and π-bonded forms of the dianionic TCNQ dimers are shown.

$[TCNQ]_2^{2-}$ dimers are connected by a single C–C bond and its existence lowers symmetry of the σ-dimer. These dimers can be generated under conducive conditions and within an appropriate cavity. For example, the σ-dimerization of the $[TCNQ]^{-\bullet}$ anion radical can occur in aqueous solutions by increasing the concentration and decreasing the temperature or within the hydrophobic cavity of α- and β-cyclodextrins.[17a,17e,17g] We envisioned, therefore, that an appropriately sized cavity coupled with a source of reducing electrons could facilitate this dimerization. The cationic macrocycle **1**-Me_3^{3+} (Scheme 2) was designed to provide such a reactor wherein the two biphenylene linkers connecting the large porphyrin to the smaller pyridinium were used to infuse the cavity with extra rigidity.

Results and Discussion

The macrocycle **1**-Me_3^{3+} was synthesized under conditions of high dilution and Cu^I catalysis (Scheme 2).[13] The zinc atom was removed during the methylation process. The neutral macrocycle **1** proved insoluble in all solvents other than pyridine and dimethyl sulfoxide (DMSO). Macrocycle **1**-Me_3•$(PF_6)_3$ showed solubility in acetone and acetonitrile. Compounds **1** and **1**-Me_3•$(PF_6)_3$ were fully characterized by ^1H and ^{13}C NMR spectroscopy and mass spectrometry.

The crystal and molecular structures of **1** were determined by X-ray diffraction analyses. Single crystals of **1** were obtained by exposing the DMSO solution of **1** in air. Macrocycle **1** crystallizes in a triclinic system with a *P*–1 space group with two molecules in a unit cell. In the crystal structure of **1** (Figure 2), the two phenylene groups attached to the porphyrin ring have dihedral angles of 53 and 60°. The two biphenylene linkers are in different environments. One interacts with the porphyrin ring in an intramolecular edge-to-face manner, whereas the other helps to form one side of a 9.5×5.0 Å cavity. The crystal structure confirmed that the relatively rigid cavity formed by one biphenylene can incorporate the anion-binding sites (triazole CH), an environment for π–π stacking (biphenylene) and the nearby catalytic porphyrin. The ^1H NMR spectrum of **1**-Me_3•$(PF_6)_3$ was assigned based on the 2D COSY and ROESY spectra (see



Scheme 2. Preparation of **1** and **1**-Me_3•$(PF_6)_3$. DBU = 1,8-diaza[5.4.0]bicycloundec-7-ene.

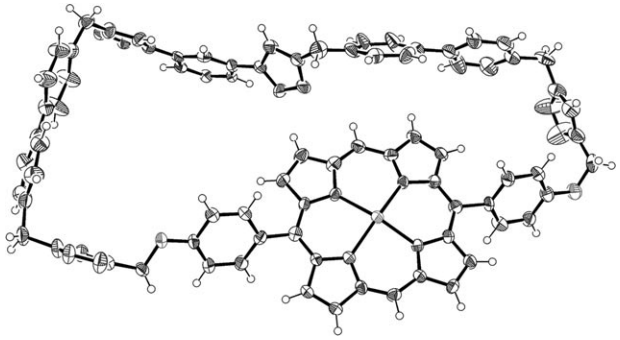


Figure 2. Molecular structure of **1** (ORTEP drawing, 50% probability level).

Figures S1–S2 in the Supporting Information), which indicated that the pyridyl ring and the two triazoles next to the porphyrin were methylated (Scheme 2).

The receptor can bind anionic species with the aid of the pyridinium and 1,2,3-triazolium cations. When halides were added to the acetonitrile solution of **1**-Me_3·$(PF_6)_3$, the resulting complexes precipitated out. The higher solubility of the complex formed between **1**-Me_3·$(PF_6)_3$ and acetate provided an opportunity to study the binding behavior in detail. With the addition of acetate, a shoulder (425 nm) on the Soret band of the porphyrin increased and reached its maximum intensity at about one equivalent (see Figure S4 in the Supporting Information). In addition, a shoulder at 365 nm appeared gradually during the addition of three equivalents of acetate. Job's plots generated at 365 nm (see Figure S5a in the Supporting Information) showed that **1**-Me_3·$(PF_6)_3$ formed complexes with three acetate anions. The resulting complex should also influence the porphyrin unit on account of proximal electrostatic interactions. Consistently, the shoulder peak at 425 nm and the partially quenched emission of the porphyrin by about 40% (see Figure S6 in the Supporting Information) is attributed to this effect.

An NMR titration also indicates that the first acetate binds with the pyridinium–bistriazole site followed by binding of two more acetate anions with the two triazolium cations. Upon addition of acetate, the pyridinium (H^o), the triazole (H^n), and the triazolium (H^g) protons of **1**-Me_3^{3+} were significantly shifted downfield as a result of the formation of hydrogen bonding between the components of the macrocycle and the acetate anions (see Figure S7 in the Supporting Information). Upon the addition of the first equivalent of acetate, the proton H^n of the two triazoles connected to the pyridinium shifted ($\delta = 0.77$ ppm) to a larger extent than H^g from the triazolium units near the porphyrin ($\delta = 0.14$ ppm). Compared to the first equivalent, the following two equivalents of acetate shifted the two H^n protons of the triazole by a smaller amount ($\delta = 0.56$ ppm), whereas the two H^g protons of the triazole shifted by a relatively bigger amount ($\delta = 0.33$ ppm; see Figure S8 in the Supporting Information). This kind of binding behavior highlighted the simultaneous effect of the pyridinium cation–anion interaction and the triazole C–H···acetate hydrogen bonding.[13]

With the anion receptor qualities shown, we considered the ability of **1**-Me_3^{3+} to serve as a nanoreactor by taking advantage of the photocatalytic porphyrin. When these two anionic guests are dragged close to the cavity at the same time, their effective molarity will increase. To confirm this idea, the dimerization of the $[TCNQ]^{-\bullet}$ radical anion by **1**-Me_3^{3+} and light in organic media was shown.

The iodide salt of **1**-Me_3^{3+} was used on account of the known reduction of TCNQ by the iodide salt of pyridinium.[22] The dimerization is readily demonstrated (Figure 3a)

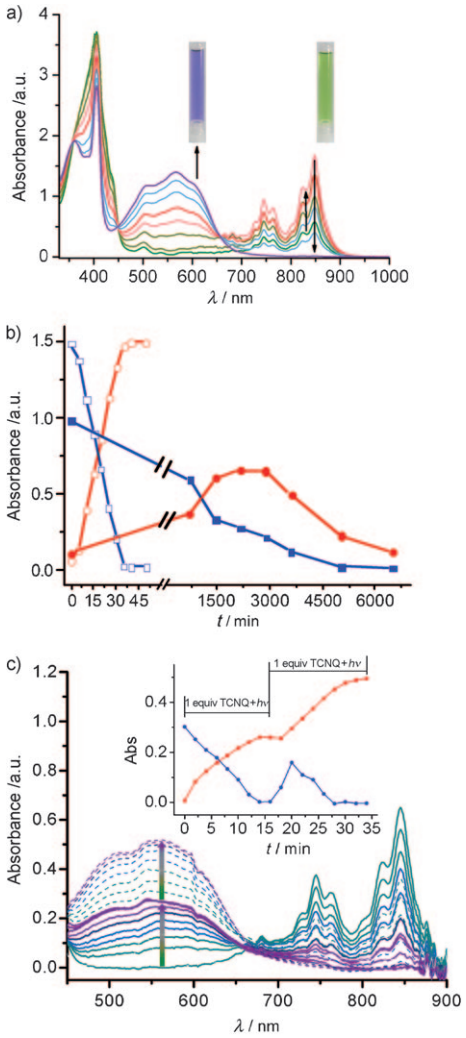


Figure 3. a) UV/Vis–NIR spectroscopic changes in an acetone solution of [**1**-Me_3-TCNQ]$^{2+}$ (12 μM) in the presence of ten equivalents of TCNQ and 10 equivalents of TBAI by using irradiation with 400 nm light, every 5 min ($l = 1$ cm; temperature: 25°C). The inset shows the representative color change of the [**1**-Me_3-TCNQ]$^{2+}$ solution before and after the irradiation. b) The absorption changes at 580 (red empty circles: light, red filled circles: dark) and 764 nm (blue empty squares: light, blue filled squares: dark) of a solution of **1**-Me_3^{3+}·$3I^-$ with 10 equivalents of $[TCNQ]^{-\bullet}$ both with and without irradiation. c) Vis–NIR changes in deaerated acetone solution of **1**-Me_3^{3+}·$3I^-$ (20 μM) with two equivalents of TCNQ upon irradiation (——), then after another two equivalents of TCNQ+TBAI (-----) and continued irradiation (the absorption of porphyrin in this region was subtracted). Inset: red squares: 580 nm, blue circles: 764 nm).

when 10 equivalents of TCNQ and 10 equivalents of tetrabutylammonium iodide (TBAI) were added to a suspension of **1**-Me_3^{3+}·3I (12 μM) in acetone. An initially yellow/orange suspension clarified and became yellow green. This yellow/green solution was analyzed from its UV/Vis–NIR spectra (dark green trace in Figure 3a) to originate from a 1:1 mixture of **1**-Me_3^{3+} and $[TCNQ]^{-\bullet}$ with the nine equivalents of TCNQ remaining unreduced in solution. We believe a complex [**1**-Me_3-TCNQ]$^{2+}$ is ultimately formed under these conditions but the radical character precluded an NMR spectroscopic study. The absorptions showed the characteristic bands of the porphyrin (≈400 nm) and the $[TCNQ]^{-\bullet}$ anion radical (650–900 nm). Furthermore, a shoulder appears at 425 nm, which is consistent with the electrostatic interaction between the complexed anion and the porphyrin as observed with acetate, that is, formation of [**1**-Me_3-TCNQ]$^{2+}$. Upon irradiation into the Soret band with 400 nm light, the radical bands of $[TCNQ]^{-\bullet}$ in the 650–900 nm region grow in to reach a maximum after 15 min (pink trace) and the shoulder at 425 nm gradually disappears. At the same time a new absorption band centered at 580 nm continuously grows in. This visible band is blueshifted from the reported σ-dimer absorption recorded in aqueous media (647 nm).[17a,d] The purple species generated by the irradiation was sufficiently stable under air to remain unchanged for more than one day at room temperature. We note that further irradiation for 90 min caused the disappearance of the 580 nm band and the appearance of the monoanionic form of the carbonyl species α,α-dicyano-*p*-toluoylcyanide ($DCTC^-$, Figure 1)[18] with a peak at 488 nm (see Figure S9 in the Supporting Information). This reaction could be prevented by deaerating the solution with argon.

The photogenerated product was analyzed to confirm its identity as the σ-$[TCNQ]_2^{2-}$ dimer. ESI-MS shows fragment ions from a $[TCNQ]_2^{2-}$ dimer appearing after the solution is irradiated with light (see Figures S10 and S11 in the Supporting Information). When the 1:1 complex [**1**-Me_3-TCNQ]$^{2+}$ in [D_6]acetone was irradiated, the ^{1}H NMR spectrum showed the appearance of an A_2X_2 spin system in the downfield region ($\delta = 7.04$, 5.23 ppm; see Figure S12 in the Supporting Information). These signals are assigned to the two ring protons in the σ-$[TCNQ]_2^{2-}$ dimer with nonequivalent *para* substituents rather than the equivalent substitutions in the parent TCNQ or from a π dimer.[17g] The IR spectra of the solutions at different stages through the experiment showed the typical features found in other TCNQ compounds.[19] The most significant bands for the parent TCNQ are $\tilde{\nu}$(CN) at 2228 and $\tilde{\nu}_{50(b3u)}$ at 860 cm^{-1}. These bands shift to lower frequencies on increasing the partial or full electronic charge on the TCNQ.[20] Consistently, the initial 1:1 complex [**1**-Me_3-TCNQ]$^{2+}$ shows a cyano band at 2181 cm^{-1}. The IR spectrum of the purple solution generated after irradiation showed different features that are attributable to the formation of an σ bond between the two $[TCNQ]^{-\bullet}$ anions (see Figure S13 in the Supporting Information). After irradiation, the 2181 cm^{-1} band from the $[TCNQ]^{-\bullet}$ radical splits into two bands at lower energy with one shifted to 2157 cm^{-1} and a second band appearing at 2130 cm^{-1}, which is a much lower value relative to those usually found in the anion radical. One shoulder peak at 794 cm^{-1} is located close to the 807 cm^{-1} band, which has been suggested as characteristic of the σ-dimer.[21]

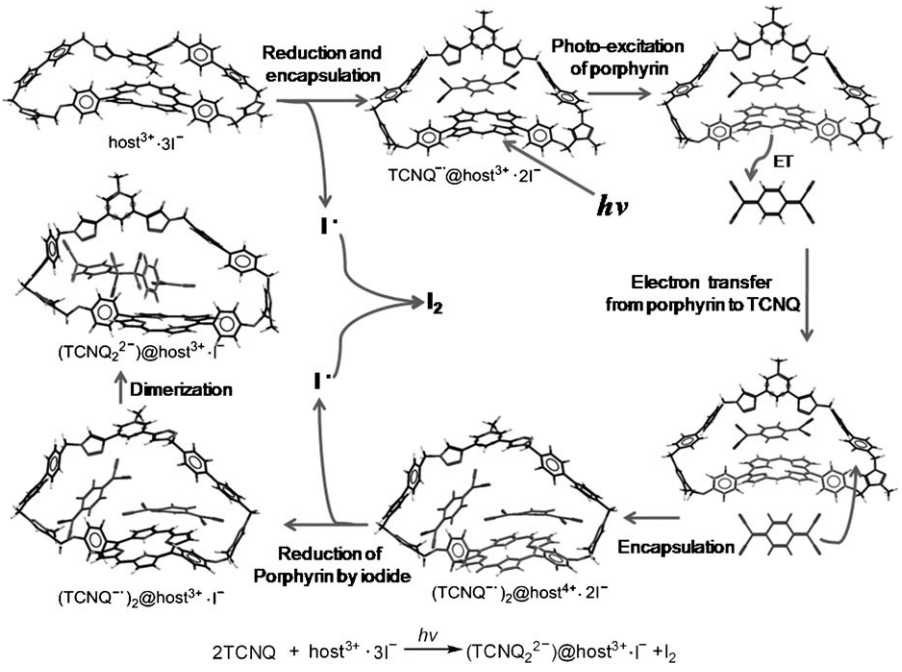
To clarify the mechanism for the photosensitized dimerization, some control experiments were performed. To test for the importance of the guest's binding to the macrocycle, a solution of the noncationic species **1** with the zinc ion removed (free-base porphyrin) was prepared and when the solution was irradiated in the presence of TCNQ (10 equiv), the direct appearance of the anionic $DCTC^-$ species was observed without dimerization. Second, when a mixture of free base **1** and three equivalents of the pre-reduced $[TCNQ]^{-\bullet}$ anion radical (see Figure S14 in the Supporting Information) was irradiated, no dimerization occurred. These results indicate that the cationic form of the receptor **1**-Me_3^{3+} is required to generate the σ-dimer. We attribute this requirement to the importance of binding the anion around the cavity.

To identify the roles played by the porphyrin, a control experiment was conducted in which 10 equivalents of pre-reduced $[TCNQ]^{-\bullet}$ anion radical was added into a solution of **1**-Me_3^{3+}·3I^- and TBAI (10 equivalents) under light and dark conditions (Figure 3b and Figure S15 in the Supporting Information). The initial green solution was rapidly converted (≈35 min) into the purple solution of the dimer. Keeping the green acetone solution in the dark at room temperature also induced the generation of the same σ-$[TCNQ]_2^{2-}$ dimer, albeit much more slowly (two days in the dark). Moreover, after only 50% conversion, the σ-dimer degrades into a colorless species (Figure 3b and Figure S16 in the Supporting Information). This particular control experiment indicated that irradiation of the porphyrin unit increases the dimerization rate by over two orders of magnitude.

The porphyrin cation can get reduced by iodide anions.[23] A control experiment was also performed to elucidate the roles played by the iodide. Thus, adding two equivalents of neat TCNQ to a suspension of **1**-Me_3^{3+}·3I^- in acetone resulted in a familiar looking yellow/green solution. The intensity of the characteristic NIR bands ($\varepsilon_{764} = 15000\ M^{-1}cm^{-1}$) for the 1:1 [**1**-$Me_3$-TCNQ]$^{2+}$ complex from this solution (Figure 3c) is close to that observed when one equivalent of the pre-reduced $[TCNQ]^{-\bullet}$ anion radical was added. Irradiation of the reactor with one equivalent of $[TCNQ]^{-\bullet}$ around leads to dimerization. Addition of another two equivalents of TCNQ to this solution does not directly show the appearance of a second $[TCNQ]^{-\bullet}$ anion until the solution is irradiated (Figure 3c, inset). This observation suggests that photoinduced electron transfer from the porphyrin to the TCNQ is required to generate the radical anion. Further irradiation does not induce the appearance of dimerization. Addition of two equivalents of iodide to this solution facilitates the dimerization (Figure 3c, inset). This observation suggests that iodide is required to reduce the porphyrin cation. Concomitantly, a further dimer is formed under these illuminated conditions. As expected, therefore, the absorption band of

the dimer, at around 580 nm, doubles in intensity (Figure 3c). The continued generation of product in this and the prior experiment with excess unreduced TCNQ (9 equiv) indicated that there is no product inhibition. Therefore, the receptor can accelerate the dimerization of both the pre-reduced $[TCNQ]^{-\bullet}$ anion radical and the one generated in situ when 400 nm light and iodide is available.

On the basis of the results and control studies, we propose the following steps for the catalytic mechanism (Scheme 3): 1) The $[TCNQ]^{-\bullet}$ anion radical pre-reduced or reduced in situ formed a 1:1 host–guest [**1**-Me_3-TCNQ]$^{2+}$ complex, 2) photochemical excitation of the porphyrin unit in the reactor, 3) this is followed by photoinduced electron transfer from the excited porphyrin unit to a neutral TCNQ (either outside or inside the receptor), giving rise to a porphyrin radical cation and a second $[TCNQ]^{-\bullet}$ radial anion, 4) the second $[TCNQ]^{-\bullet}$ is dragged close to the cavity with the help of the electrostatic stabilization provided by the triazolium cations, 5) the two $[TCNQ]^{-\bullet}$ anion radicals constrained around the cavity rapidly formed the σ-dimer, 6) at some point (either before or after the constraining of the second $[TCNQ]^{-\bullet}$ anion radical), the photogenerated porphyrin cation gets reduced by iodide, and 6) the σ-dimer is either ejected from the host or is displaced by the $[TCNQ]^{-\bullet}$ anion radical. The receptor can accelerate the dimerization of at least 10 equivalents of TCNQ, thus indicating that this receptor can bring together two reactants to accelerate a reaction, and turnover like a catalyst.



Scheme 3. Proposed mechanism of the photochemically induced dimerization of TCNQ by **1**-Me_3^{3+} (the $[TCNQ]^{-\bullet}$ might sit in the cavity or outside the cavity, but it is constrained around the pyridinium or triazolium centers by electrostatic interactions, here only the inside case was shown).

Conclusion

We describe a nanometer-sized macrocyclic receptor based on a photoactive porphyrin unit and anion-binding pyridinium and triazolium units that was prepared by using the ubiquitous "click chemistry". The potential of this structure to act as a reactor was confirmed by the photodriven dimerization of TCNQ. There is clear evidence for a rate increase of over two orders of magnitude, photosensitization of the host, and demonstrated turnover of the catalyst. These results for the first time show the construction of cationic receptors that can host anionic species and sensitize their reaction. This approach is of great significance for the development of novel nanoscale devices capable of supramolecular catalysis.

Experimental Section

General methods: All reagents were obtained from commercial suppliers and used as received unless otherwise noted. Column chromatography was performed on silica gel (160–200 mesh) and TLC was performed on precoated silica gel plates and observed under UV light. NMR spectra were recorded on Bruker Avance DPS-400 and Bruker Avance DPS-600 spectrometers at room temperature (298 K). Chemical shifts were referenced to the residual solvent peaks. MALDI-TOF mass spectrometry was performed on a Bruker Biflex III mass spectrometer. Electronic absorption spectra were measured on a JASCO V-579 spectrophotometer. Fluorescence excitation and emission spectra were recorded by using a Hitachi F-4500. All single-crystal X-ray diffraction data were collected on a Rigaku Saturn X-ray diffractometer with graphite-monochromator $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 173 K. Intensities were corrected for absorption effects by using the multiscan technique SADABS (Siemens Area Detector Absorption Corrections). The structures were solved by direct methods and refined by a full-matrix least-squares technique based on F2 by using SHELXL 97 program (Sheldrick, 1997). The extended packing plots and data from crystal packing were obtained by using the software Mercury 1.4.1. Compounds **3** and **5** were synthesized in accordance with literature procedures.[24,25]

Compound 2: K_2CO_3 (0.55 g, 4 mmol) and 3-bromopropyne (0.354 g, 3 mmol) were added to a solution of **5** and 15-bis(4-hydroxyphenyl)porphyrin[26] (0.556 g, 1 mmol) in DMF (20 mL) and the solution was heat to 70 °C for 10 h. DMF was removed under vacuum. The mixture was washed with water and the aqueous solution was extracted with CH_2Cl_2 (3×50 mL). The organic layer was separated, dried over $MgSO_4$, filtered, concentrated under reduced pressure, and the resulting crude was purified by column chromatography (CH_2Cl_2 containing 0.5% pyridine as eluent) to give **2** (0.49 g, yield: 78%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 10.16$ (s, 2H), 9.32 (d, $J = 4$ Hz, 4H), 9.06 (d, $J = 4$ Hz, 4H), 8.14 (d, $J = 8$ Hz, 4H), 7.35 (d, $J = 8$ Hz, 4H), 4.97 (s, 4H), 2.69 ppm (s, 2H); ^{13}C NMR (100 MHz, [D_6]DMSO, 25 °C, TMS): $\delta = 157.66$, 150.32,

149.96, 149.66, 136.33, 136.21, 132.80, 132.46, 119.36, 113.93, 106.79, 80.33, 79.36, 56.62, 40.97, 40.76, 40.55, 40.35, 40.14, 39.93, 39.72, 0.91 ppm; MS (MALDI-TOF): m/z: calcd for $C_{38}H_{24}N_4O_2Zn$: 632.12 $[M]^+$; found: 632.5; elemental analysis calcd (%) for $C_{38}H_{24}N_4O_2Zn$: C 71.99, H 3.82, N 8.84; found: C 71.86, H 3.89, N 8.79.

Compound 4: A solution of **2** (316 mg, 0.5 mmol), 4,4′-bis(azidomethyl)-biphenyl (**3**)[24] (528 mg, 2 mmol), and DBU (4.0 mmol, 0.7 mL) in toluene (50 mL) was degassed (argon) for 30 min and heated to 70 °C while flushing with argon. At 70 °C, CuI (0.02 mmol, 3.8 mg) was added to the mixture. The mixture was stirred for 4 h under argon. The mixture was concentrated in vacuo. The product was purified by chromatography (SiO_2, CH_2Cl_2/methanol 20:1) to afford **4** (522 mg, 90 % yield) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 10.14 (s, 2H), 9.30 (d, J = 4 Hz, 4H), 9.03 (d, J = 4 Hz, 4H), 8.11 (d, J = 8 Hz, 4H), 7.61 (s, 2H), 7.60 (d, J = 8 Hz, 4H), 7.52 (d, J = 8 Hz, 4H), 7.40 (d, J = 4 Hz, 4H), 7.33 (d, J = 8 Hz, 4H), 7.28 (d, J = 8 Hz, 4H), 5.64 (s, 4H), 5.49 (s, 4H), 4.29 ppm (s, 4H); ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 158.32, 150.27, 149.55, 140.23, 140.06, 139.41, 136.17, 135.88, 135.72, 132.67, 132.40, 129.77, 129.38, 127.86, 127.72, 119.39, 113.78, 106.66, 62.17, 53.97, 53.36, 40.94, 40.73, 40.52, 40.31, 40.10, 39.89, 39.69, 36.50, 35.19, 31.49, 30.87, 30.62, 29.74 ppm; MS (MALDI-TOF): m/z: calcd for $C_{66}H_{48}N_{16}O_2Zn$: 1161.34 $[M]^+$; found: 1161.1 $[M+H]^+$, 1135.1 $[M+2H-2N]$; compound **4** was also characterized by X-ray diffraction analysis (see Section S5 in the Supporting Information).

Compound 1: DBU (4.0 mmol, 0.7 mL) was added to toluene (200 mL) and left under degassed (argon) for 30 min and then heated to 70 °C while flushing with argon. At 70 °C, CuI (0.02 mmol, 3.8 mg) was added to the mixture. A solution of **5**[25] (12.7 mg, 0.1 mmol) and **4** (116 mg, 0.1 mmol) in THF (5 mL) and toluene (30 mL) was added to the solution slowly over 10 h and then the mixture was stirred for another 4 h under argon. The mixture was concentrated in vacuo. The product was purified by chromatography (SiO_2, CH_2Cl_2/pyridine/methanol 100:1:3) to afford **1** (84 mg, 65 % yield) as a purple solid. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 10.25 (s, 2H), 9.37 (d, J = 4.4 Hz, 4H), 8.97 (d, J = 2 Hz, 2H), 8.86 (d, J = 4.4 Hz, 4H),8.76 (s, 2H), 8.59 (d, J = 2 Hz 1H), 8.46 (s, 2H), 8.04 (d, J = 8.4 Hz, 4H), 7.72 (d, J = 8.4 Hz, 4H), 7.61 (d, J = 8.4 Hz, 4H), 7.47 (d, J = 8.4 Hz, 4H),7.43 (d, J = 8.4 Hz, 4H), 7.29 (d, J = 8.4 Hz, 4H), 5.77 (s, 4H), 5.63 (s, 4H), 5.60 ppm (s, 4H); ^{13}C NMR (150 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 157.43, 150.00, 149.92, 149.23, 146.03, 144.13, 144.04, 139.92, 136.62, 136.02, 135.78, 135.57, 135.35, 132.38, 132.05, 129.15, 129.07, 127.65, 127.62, 127.23, 125.37, 124.37, 123.10, 119.05, 114.16, 106.36, 61.69, 53.27, 53.05 ppm; MS (MALDI-TOF): m/z: calcd for $C_{75}H_{53}N_{17}O_2Zn$: 1287.39 $[M]^+$; found: 1289.6 $[M+2H]^+$, 1352.5 $[M+H+Cu]^+$.

Compound 1-Me$_3$·(PF$_6$)$_3$: Compound **1** (13 mg, 0.01 mmol) in DMF (3 mL) and MeI (1 mL) was heated at 40 °C overnight. The mixture was then poured into CH_2Cl_2 (50 mL) to give some precipitate, which was washed with CH_2Cl_2. The solid was suspended in acetone, NH_2PF_6 (5 equiv) was added, and the mixture became a clear solution. The solvent was removed, washed the with water, and dried under vacuo to give **1**-Me$_3$·(PF$_6$)$_3$ (16.8 mg, 95 %). ^{1}H NMR (400 MHz, CD_3CN, 25 °C, TMS): δ = 10.41 (s, 2H), 9.49 (d, J = 4 Hz, 4H), 8.99 (d, J = 4 Hz, 4H), 8.79 (s, 2H), 8.77 (s, 1H), 8.40 (s, 2H), 8.14 (d, J = 8 Hz, 4H), 7.85 (s, 2H), 7.56 (d, J = 8 Hz, 4H), 7.52 (d, J = 8 Hz, 4H), 7.40 (d, J = 8 Hz, 4H), 7.02 (d, J = 8 Hz, 4H), 6.43 (d, J = 8 Hz, 4H), 5.85 (s, 4H), 5.69 (s, 4H), 5.45 (s, 4H), 4.68 (s, 4H), 4.49 (s, 6H), 4.19 (s, 3H), −3.31 ppm (s, 2H); ^{13}C NMR (100 MHz, CD_3CN, 25 °C, TMS): δ = 157.80, 148.35, 146.36, 142.35, 142.00, 140.71, 137.28, 136.62, 134.81, 133.49, 132.62, 132.05, 131.06, 130.82, 129.97, 129.07, 128.17, 124.45, 119.52, 116.18, 106.73, 60.46, 58.24, 54.26, 40.07, 31.25 ppm; HRMS (ESI): m/z: cald for $C_{78}H_{64}N_{17}O_2$: 423.51265 $[M]^{3+}$; found: 423.51272 $[M]^{3+}$.

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