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From the Decks to the Bridges: Optoelectronics in [2.2]Paracyclophane Chemistry

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In this microreview, we highlight optical properties of [2.2]paracyclophanes (pCps). We demonstrate how the spectroscopic properties that stem from the strained and π-stacked structure have resulted in pCps being incorporated in materials science and polymer synthesis. As a result of chromophore substitution, internal charge transfer (ICT) between the two rings of the cyclophane core produce frameworks with unique optical properties. Deck-substituted molecules and polymers have beensynthesized that possess donor and acceptor groups that affect internal charge transfer (ICT). We also demonstrate that bridge-substituted [2.2]paracylophanes, although not well studied in this context, display unexpected optical properties owing to nonconventional ICT. A highlight is a recent templated solid-state synthesis that affords a pCp that exhibits dramatic red-shifted fluorescence.

Introduction

Much interest has been focused on the designed synthesis of molecular architectures that place chromophores into well-defined geometries.[1] [2.2]Paracyclophane (pCp) is a key building block in this regard, as the molecule provides an aromatic scaffold that can impart unique structural and physical properties on a variety of functional groups. Indeed, the phane supports a 3D structure combined with transannular properties that organic and materials chemists have sought to develop as an organic building block in the engineering of complex molecules and materials.

From a fundamental standpoint, pCp is composed of two benzene rings covalently fixed in a face-to-face geometry by ethano bridges. As demonstrated by crystal structure studies, the two rings of pCp are stacked and distorted into a boat orientation (Scheme 1).[2] The structural aberration, coupled with intrinsic transannular effects, has resulted in pCps with unique reactivity and intriguing spectroscopic properties.[3] Initially, pCp was coined an aromatic molecule *par excellence*, with studies aimed to understand how changes in molecular structure upon simple aromatic substitution affect reactivity, physical, and spectroscopic properties. More recently, pCp has been engineered as a core for functionalization with applications in organometallic and asymmetric synthesis,[4] as well as organic scaffolds.[5] The scaffolds have invariably involved heavy substitution of the

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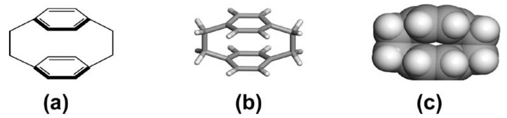
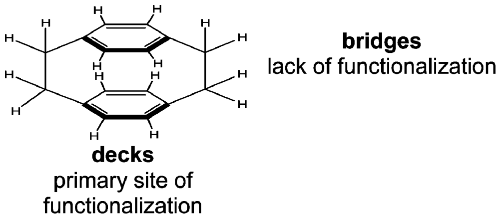
aromatic decks, leaving the aliphatic bridges largely empty. Additional studies have focused on the synthesis of pCp derivatives[6] and frameworks utilized for cycloadditions.[7]

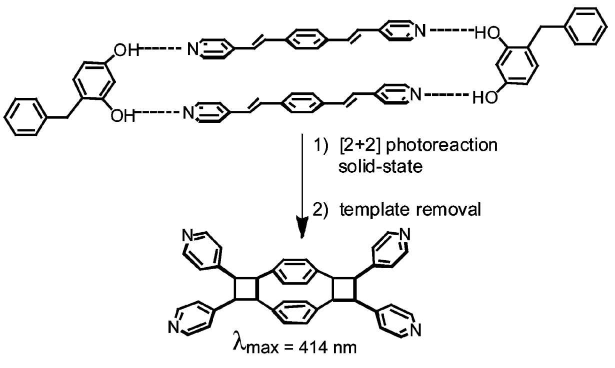


Scheme 1. (a) [2.2]Paracyclophane and (b–c) crystal structures showing the stacked aromatic rings and boat-like orientation.

In this review, we provide a survey of pCps with a focus on optical properties that result from functionalization of the aromatic decks and bridges (Scheme 2). Our recent work has led to interests in developing pCps with unique optical properties. The work stems from a templated solid-state synthesis that produces bridge-substituted pCps (Scheme 3).[8] The synthesis of the functionalized pCp contrasts the majority of known methods that affect deck substitution. Here, we will give a detailed classification of both deck- and bridge-substituted pCps and corresponding optical properties. We will show that the development of pCp-based molecular chromophores and related polymers typically relies on substitution of the stacked aromatic core. The synthesis of the deck-substituted pCps is carried out in a divergent methodology, wherein conjugation of the pCp core is extended through synthetic coupling methods. As a result of chromophore elongation, pCp demonstrates a prominent intermolecular charge transfer (ICT) responsible for an optical output.[9] We will also describe our method that produces a pCp core with substituents on the distal bridges via a convergent design. We rely on the use of small molecule templates to organize functionalized diene chromophores in a geometry suitable for a double [2+2] photoreaction.[10] The reaction produces a pCp dimer stereospecifically, quantitatively, and in gram quantities. From our experiments, we will show how bridge substitution can be exploited – despite a saturated connection – to affect fluorescence of the pCp core.



Scheme 2. Functionalization sites of pCp.



Scheme 3. Templated solid-state synthesis of a bridge-substituted pCp.

Optical Properties of [2.2]Paracyclophane

pCp, and derivatives, have defined a rich area of inquiry for over 60 years.[11] The foundation lies in the unusual structure of pCp, and hence, unique and novel properties that can result from interactions within the strained architecture. In recent years, pCp has been utilized as a model to study electron delocalization, owing to the two co-facially stacked benzene rings being held in place via aliphatic bridges.[12] Unique optical properties are observed when two or more π-systems are geometrically fixed in close proximity in a molecule such as pCp. In particular, transannular through-space and through-bond donation perturb the molecular π orbitals such that σ(bridge)···π(deck) interactions can lead to modulated donor–acceptor interactions.

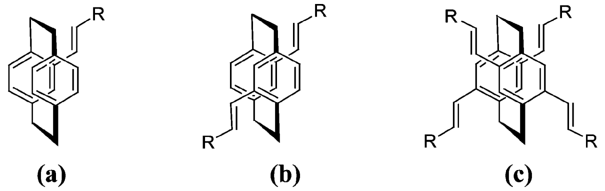
It is well known that pCp alone exhibits an abnormal absorbance spectrum compared to simple benzene derivatives and related hydrocarbons, exhibiting absorbance bands at 225 nm, 244 nm, 286 nm, and 302 nm. The long-wavelength band has been coined the "cyclophane band," as the band is well past the absorption of simple alkyl aromatics.[5] The emission spectrum of pCp is also unexpected, when compared to alkyl aromatics, as a broad band is observed at 356 nm. The spectroscopic properties are attributed to strong σ-π interactions,[13] as well as a π-π through-space delocalization that result in energy transfer throughout the entire cyclophane core.[12]

Owing to the unique optical properties conferred by the covalently stacked aromatic rings, pCp has emerged as a prominent organic building block for the development of novel device-based applications.[14] There is an expectation that perturbations in the molecular structure of pCp can lead to ICT that affects device performance through electronic communication. In particular, extension of the end-to-end conjugation length generates pCps with excitations and emissions up to 430 and 530 nm,[15] respectively. Termination of the chromophore with acyclic donor and acceptor groups also enhances the ICT, with absorbances and emissions near 500 and 600 nm, respectively.[9,17,19,20] Enhancement of ICT is also seen in pCp-based polymers. Polymeric systems display ICT with absorbances up to 470 nm and emissions up to 600 nm.[25–28,30,32,34–38] The changes to molecular structure, coupled with the unique structure of pCp, have produced architectures that show tunable optoelectronic properties that can lead to device-based applications.

In more general terms, understanding how molecular structure correlates to bulk properties is important when designing electronic devices. Organic semiconductors and conjugated polymers rely on the specific orientation and organization of π-networks for optimal performance. In these systems, molecular subunits are subjected to different environments that often result in poorly defined morphologies with difficult to quantify photophysical properties.[15] In this context, the design and synthesis and well-defined pCp-based chromophoric materials has been targeted as a means to probe the effect of electronic communication on optoelectronic properties, and ultimately, incorporate tailored properties to improve device performance.

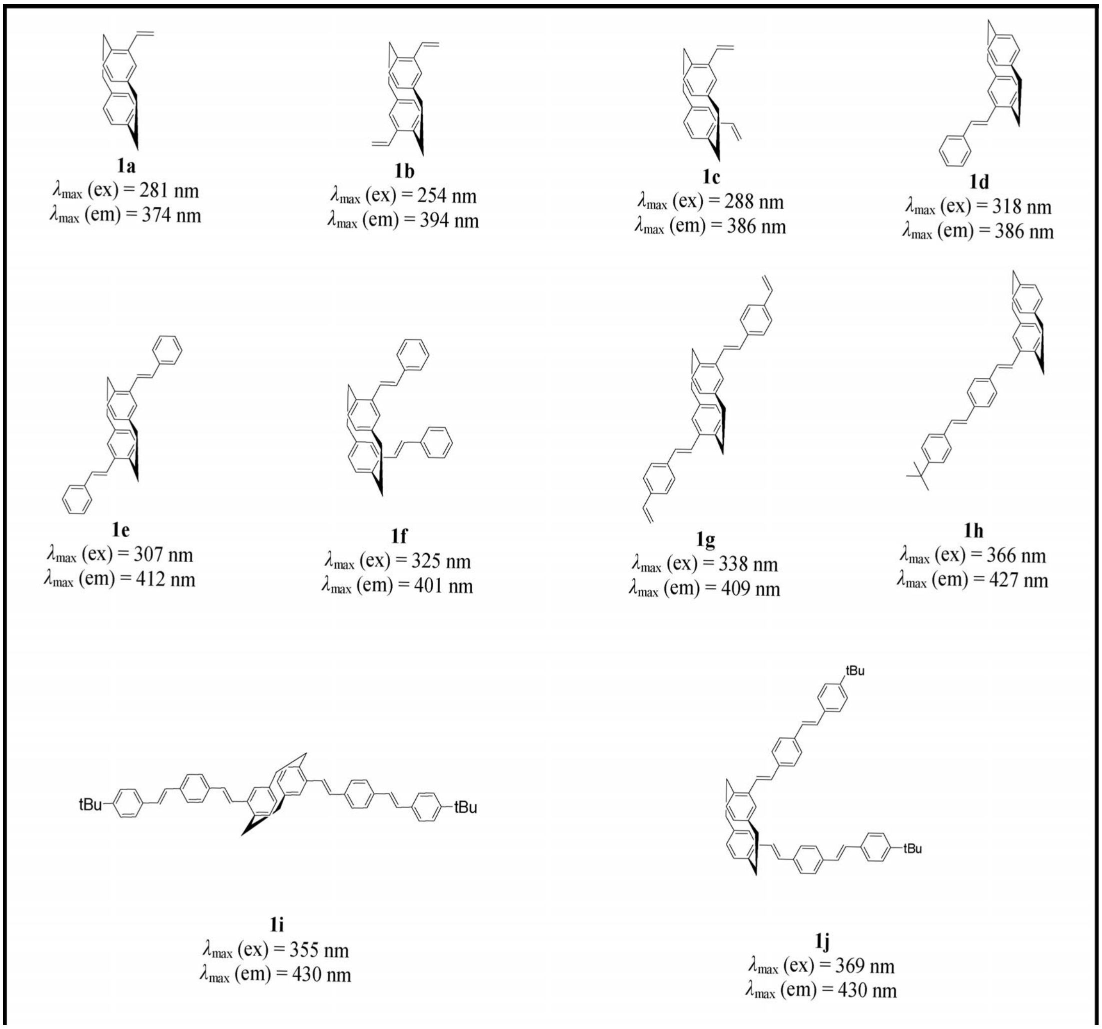
Deck-Functionalized [2.2]Paracyclophanes as Platforms to Study Optical Properties

It is well known that electronic communication between chromophoric subunits depends on relative orientations and through-space distance. By exploiting the strained structure of pCp, and coupling chromophores orthogonally to the decks, conjugated frameworks have been developed that enhance ICT and lead to varied photophysical properties. Compounds that demonstrate ICT have possessed distinct donor and acceptor groups typically connected by a π-electron conjugated path. Pioneering work involving pCp has been accomplished by Bazan and co-workers through the synthesis of several pCps wherein stilbene-based donor and/or acceptor units have studded the pCp decks (Scheme 4). By coupling stilbenes to pCp, a family of molecules has been generated that provide a foundation to study the perturbations of optical properties as a function of molecular structure (Table 1). By using well-known organic chromophores such as stilbenoids, comparisons have been made between a "monomer" and pCp-based "dimer". Specifically, the molecular orbitals of the pCp dimer are generally known to split into symmetric and antisymmetric



Scheme 4. Deck-substituted pCps studied by Bazan and co-workers.[16]

Table 1. pCp-Based chromophoric scaffolds with relevant optical properties.



1a
λ_{max} (ex) = 281 nm
λ_{max} (em) = 374 nm

1b
λ_{max} (ex) = 254 nm
λ_{max} (em) = 394 nm

1c
λ_{max} (ex) = 288 nm
λ_{max} (em) = 386 nm

1d
λ_{max} (ex) = 318 nm
λ_{max} (em) = 386 nm

1e
λ_{max} (ex) = 307 nm
λ_{max} (em) = 412 nm

1f
λ_{max} (ex) = 325 nm
λ_{max} (em) = 401 nm

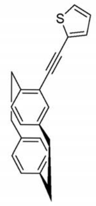
1g
λ_{max} (ex) = 338 nm
λ_{max} (em) = 409 nm

1h
λ_{max} (ex) = 366 nm
λ_{max} (em) = 427 nm

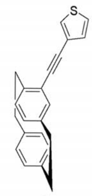
1i
λ_{max} (ex) = 355 nm
λ_{max} (em) = 430 nm

1j
λ_{max} (ex) = 369 nm
λ_{max} (em) = 430 nm

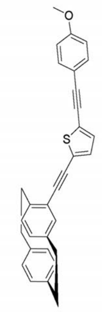
Table 1. *(continued)*.



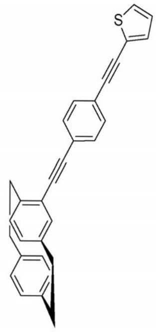
2a
λ_{max} (ex) = 319 nm
λ_{max} (em) = 377 nm



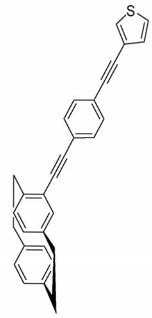
2b
λ_{max} (ex) = 299 nm
λ_{max} (em) = 334 nm



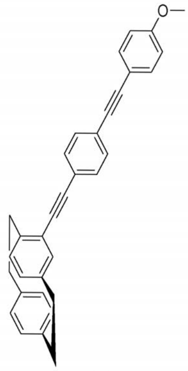
2c
λ_{max} (ex) = 362 nm
λ_{max} (em) = 422 nm



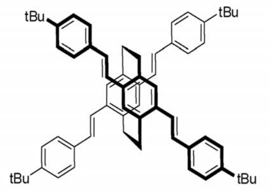
2d
λ_{max} (ex) = 340 nm
λ_{max} (em) = 395 nm



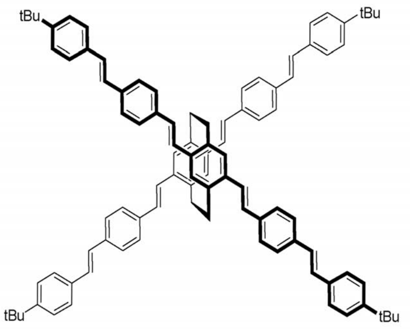
2e
λ_{max} (ex) = 330 nm
λ_{max} (em) = 381 nm



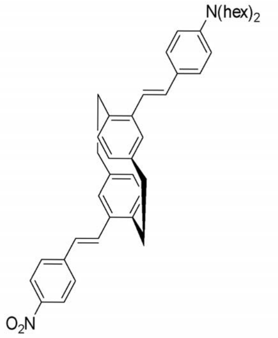
2f
λ_{max} (ex) = 336 nm
λ_{max} (em) = 389 nm



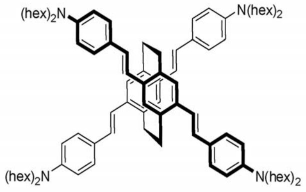
3a
λ_{max} (ex) = 380 nm
λ_{max} (em) = 450 nm



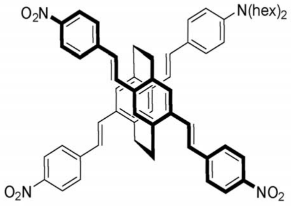
3b
λ_{max} (ex) = 429 nm
λ_{max} (em) = 510 nm



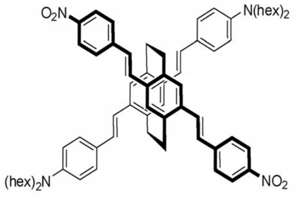
4
λ_{max} (ex) = 383 nm
λ_{max} (em) = 570 nm



5a
λ_{max} (ex) = 440 nm
λ_{max} (em) = 540 nm

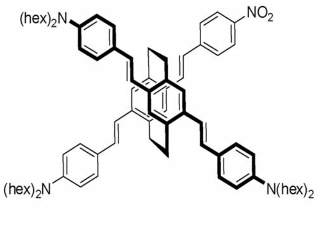


5b
λ_{max} (ex) = 417 nm
λ_{max} (em) = 570 nm

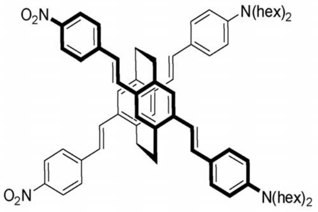


5c
λ_{max} (ex) = 417 nm
λ_{max} (em) = 690 nm

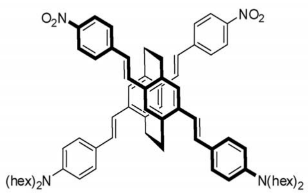
Table 1. *(continued)*.



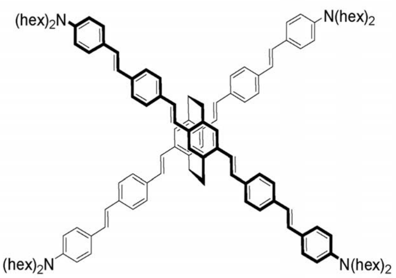
5d
λ_{max} (ex) = 440 nm
λ_{max} (em) = 540 nm



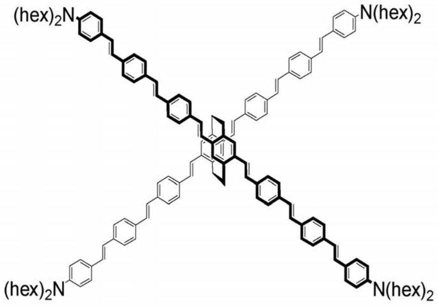
5e
λ_{max} (ex) = 470 nm
λ_{max} (em) = 555 nm



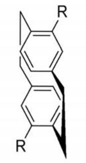
5f
λ_{max} (ex) = 460 nm
λ_{max} (em) = 545 nm



6a
λ_{max} (ex) = 457 nm
λ_{max} (em) = 510 nm

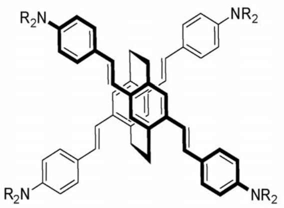


6b
λ_{max} (ex) = 454 nm
λ_{max} (em) = 520 nm



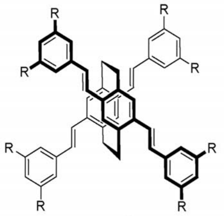
R = $(CH_2)_6\overset{\oplus}{N}Me_3\ \overset{\ominus}{Br}$

7a
λ_{max} (ex) = 200 nm
λ_{max} (em) = 352 nm



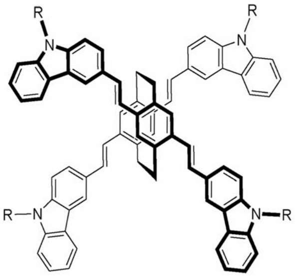
R = $(CH_2)_6\overset{\oplus}{N}Me_3\ \overset{\ominus}{I}$

7b
λ_{max} (ex) = 435 nm
λ_{max} (em) = 553 nm



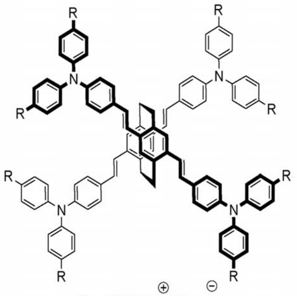
R = $(CH_2)_6\overset{\oplus}{N}Me_3\ \overset{\ominus}{Br}$

7c
λ_{max} (ex) = 392 nm
λ_{max} (em) = 496 nm



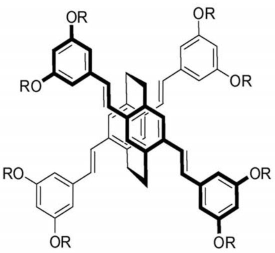
R = $(CH_2)_6\overset{\oplus}{N}Me_3\ \overset{\ominus}{I}$

8a
λ_{max} (ex) = 410 nm
λ_{max} (em) = 505 nm



R = $(CH_2)_6\overset{\oplus}{N}Me_3\ \overset{\ominus}{I}$

8b
λ_{max} (ex) = 431 nm
λ_{max} (em) = 537 nm



R = $[(CH_2)_4SO_3][NBu_4]$

9
λ_{max} (ex) = 399 nm
λ_{max} (em) = 511 nm

contributions of the monomer that result in a smaller HOMO–LUMO gap and, thus, lower energy fluorescence compared to monomer systems. Initial studies by the Bazan group drew comparisons between pCp bound styryl-based chromophores of differing conjugation lengths (**1a**–**j**). More recent investigations have led to pCps that serve as prototypes for fluorescent sensor-based applications (i.e. biological, chemical).

Changes in Conjugation Length

pCps **1a**–**j** have provided insights on how conjugation length and molecular structure can be used to understand the effects of through-space delocalization on the optical properties of the pCp framework.[17] Vinyl-substituted **1a** was initially employed as the simplest chromophore with the shortest conjugation length. The maximum excitation for the extended derivative **1a** was determined to be 281 nm, which is surprising since pCp itself exhibits a maximum absorbance at 310 nm. Additionally, **1a** showed an emission maximum at 374 nm, which is red-shifted with respect to pCp ($\lambda_{\max}$ = 356 nm). Bazan and co-workers also examined the properties of divinyl pCps **1b** and **1c**. The pseudo-*para* derivative demonstrated a further blue shift in absorbance ($\lambda_{\max}$ = 254 nm), as well as a red shift in fluorescence ($\lambda_{\max}$ = 394) relative to both pCp and **1a**. Conversely, the pseudo-*ortho* derivative displayed a bathochromic shift in absorbance relative to **1a** at 288 nm that also corresponded to a similar bathochromic shift in fluorescence up to 386 nm. In related studies utilizing monostyryl- and distyryl-substituted pCps **1d**–**g** (Figure 1), absorbances and emissions up to 338 and 412 nm, respectively, were observed.

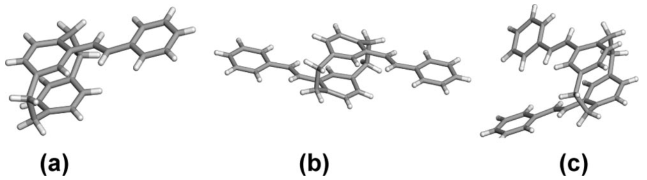


Figure 1. X-ray crystal structures of **1d**, **1e**, and **1f**, respectively.

The shifts in emissions involving **1a**–**j** were consistent with increasing the end-to-end chromophore length, which increased the ability of electronic charge to be shuttled across a longer distance.[12,17] In addition to conjugation length, substitution pattern impacted emission, as lower energy fluorescence was observed when the chromophores were arranged in the pseudo-*para* orientation, as opposed to pseudo-*ortho*. The pseudo-*para* orientation increases electronic communication between the chromophores, while influencing through-space delocalization.

Further studies on the impact of conjugation length on electronic communication were accomplished by Taticchi and co-workers. Specifically, thiophene and/or benzene rings were used to extend the conjugation of 4-ethynyl[2.2]-paracyclophane, affording pCps **2a**–**2f**.[18] Thiophene-substituted **2a** and **2b** were the simplest pCps investigated, differing only in connectivity to the thiophene. **2b** displayed excitation and emission maxima at 299 nm and 334 nm, respectively. In contrast, **2a** demonstrated red-shifted absorbance and fluorescence to 319 nm and 377 nm, respectively. These observations are consistent with improved conjugation of the β-thienyl system. The more complex **2c** was investigated to study the effect of a *p*-methoxy-ethynylbenzene chromophore attached at the periphery of the thiophene. Lengthening of the conjugation effectively resulted in red shifts in both absorbance and fluorescence of **2a** of an additional 50 nm. The benzene-based counterpart of **2c** was studied. Compound **2f** displayed a strong excitation of 336 nm, along with an emission at 389 nm. The results were considerably blue-shifted compared to thiophene-based **2c**. This can be attributed to increased electron delocalization facilitated by the thiophene rings. In related studies involving additional ethynylbenzene moieties within the pCp side chain (**2d**–**2e**), absorbances and emissions up to 340 nm and 395 nm, respectively, were observed.

Installation of Acyclic Substituents

Further perturbations to the optical properties of pCp have been achieved when a chromophore terminated in a strong acyclic donor and/or acceptor was coupled to the stacked framework. In particular, the introduction of *tert*-butyl, amine, and/or nitro functionalities resulted in architectures with more efficient (i.e. high wavelength emission) ICT owing to the placement of electron-donating or -withdrawing groups within the framework. Termination of the stilbenoid chromophores with *tert*-butyl groups, as in the cases of **1h**–**j**, resulted in absorbance maxima up to 370 nm and an emission maximum of 430 nm. Additional coupling of the *tert*-butyl styryl and stilbene-based chromophores led to tetrasubstituted donor scaffolds **3a** and **3b**.[19] The excitation spectra displayed maxima at 380 nm and 420 nm for **3a** and **3b**, respectively, while the emission spectra revealed maxima at 450 nm and 510 nm. Donor–acceptor–donor systems, such as those in **1h**–**3b**, are examples wherein electronic communication is more efficient from the donor chromophoric arms to the acceptor cyclophane core owing to the presence of strong donor groups that give rise to lower energy excitation and emission behavior.

Unlike the ITC observed with terminal donor groups, the introduction of a combination of donor and acceptor groups promoted a more efficient charge transfer, with electronic charge being favorably shuttled throughout the entire scaffold. The coupling of a *p*-(dihexylamino)styrene to one end of a substituted pCp, followed by a *p*-nitrostryryl chromophore at the other terminus, resulted in a donor–acceptor system with end-to-end conjugation (**4**).[9] An excitation maximum of 383 nm and emission maximum of 570 nm were observed for **4**.

An analogous class of tetrasubstituted pCps **5a**–**f** decorated with dihexylamino and/or nitro groups has also been reported (Figure 2).[20] The tetraamine **5a**, which consisted of *p*-(dihexylamino)styrene branches as donor groups, exhibited an absorbance at 440 nm and an excitation at 560 nm.

Comparable results were observed with either three donor or three acceptor termini (**5b** and **5d**, respectively). Compounds **5c**, **5e**, and **5f** each possessed two donor and two acceptor arms. pCps **5e** and **5f**, wherein both donor groups were placed in the pseudo-*ortho* and pseudo-*meta* positions were determined to exhibit similar absorbances up to 470 nm and emission maxima near 550 nm. Conversely, **5c** demonstrated a more unique behavior, displaying a blue-shifted absorbance at 417 nm that corresponded to two separate emission peaks at 500 nm and 690 nm. The dual emission resulted from two equally accessible excited states, owing to coupling of the stilbenoid "parent" donor and acceptor chromophores across the transannular gap. Structurally analogous 5- and 7-ring pCp dimers **6a** and **6b** were also examined, both of which displayed an absorbance up to 457 nm with emissions at 510 and 520 nm, respectively.[21] Indeed, the introduction of donor and/or acceptor groups resulted in lower energy absorbance and fluorescence owing to the strong ICT seen associated with donor–acceptor systems.

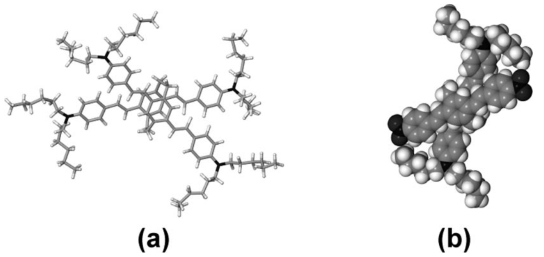


Figure 2. X-ray crystal structures: (a) perspective view of **5a** and (b) space-filling of **5c**.

Installation of Charged Groups

Applying pCp-based architectures for biological applications will likely require charged groups for water solubility. The molecules should contain strong interchromophore delocalization to be less susceptible to environmental factors (e.g. aggregation) that could affect electronic properties.[12] Efforts by Bazan to achieve water solubility led to incorporation of charged functionalities within the pCp framework.

pCps **7a–c** contain disubstituted and tetrasubstituted pCp decorated with alkyl ammonium groups.[22–23] The related neutral pCps were also studied. The disubstituted pair was studied to investigate the effect of charge with direct comparison to pCp. In general, the charged compounds displayed red-shifted absorbances and emissions relative to the neutral forms. The charged compounds were also found to exhibit solvatochromism, wherein more polar solvents (e.g. DMSO, water) provided further red shifts when compared to weakly polar solvents (e.g. THF, toluene, hexanes).

Disubstituted **7a** exhibited a maximum absorbance at 200 nm along with weaker absorbances at 227, 255, and 306 nm, which was analogous to the neutral counterpart. Excitation at 200 nm resulted in an emission at 352 nm, a slight red shift compared to the parent pCp. The optical properties of **7a** are comparable to that of pCp owing to a lack of additional chromophores and/or strong donors to increase the ICT properties. However, tetrasubstituted pCps **7b–c**, differing only by terminal groups, displayed a red-shifted shifted emission compared to neutral counterparts on the order of 20–25 nm. When *N*-substituted carbazoles were incorporated into structurally analogous **8a** and **8b**, a red-shifted fluorescence of up to 45 nm was observed. The shifts are consistent with increasing the electron accepting properties of the pendant amines via quaternization of the N-atoms. In the charged frameworks, ICT is optimized owing to increased electron donation from the pCp core outward to the electron-accepting arms of the frameworks. The positively charged N-atoms act as more efficient electron acceptors owing to overall electron deficiency. Bazan has also studied related O-based donors with charged groups. pCp **9**, which contains an ammonium sulfate moiety, displayed an absorbance of 399 nm, as well as a sharp emission at 511 nm.[24]

Studies of Bazan and Taticchi on effects of conjugation length, as well as incorporation of acyclic substituents and charged functionalities, have provided a foundation for the development of pCps with well-defined optoelectronic properties and optimized electron delocalization. Relative effects of chromophore orientation, contact site, and end-to-end conjugation length have provided an understanding of how to favorably perturb through-space delocalization and ICT to design pCp-based frameworks that provide insights into related conjugated polymers. Owing to the use of pCp as the core chromophore, and though the coupling of secondary chromophores to the core, pCp architectures were achieved that display prominent emissions. The results bode well for the further incorporation of molecular pCp derivatives in materials science as functional devices (e.g. biosensors, semiconductors, OLED materials).[12]

π-Stacked Polymers Based on Conjugated [2.2]Paracyclophane

In addition to molecules, optical properties of polymers based on pCp have been studied. Chujo and co-workers have laid a foundation by focusing on layered pCp polymers with either a 4,16-divinyl or 4,16-diethynyl[2.2]paracyclophane core. Initial studies focused on integrating pCp within a poly (*p*-phenylene-ethynylene) (PPE) or poly (*p*-phenylene-vinylene) (PPV) framework (Table 2). More recently, the focus has moved to the installation of donor and/or acceptor functionalities, similar to the molecules, within the PPE polymer backbone. To tailor properties of the polymers, donor and/or acceptor groups studied in the context of related conjugated polymers were installed along the polymeric backbone via covalent linkages to the decks of pCp. Integration of the groups has allowed for efficient electronic communication throughout the polymer, resulting in sharp emissions throughout the visible region on the order of 400 to 600 nm and promising charge-transfer properties compared to the "monomeric" conjugated polymers (Scheme 5).

Table 2. pCp-Based PPV and PPE conjugated polymers with relevant optical properties.

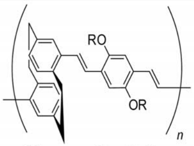
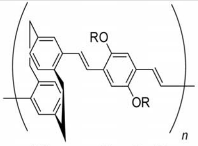
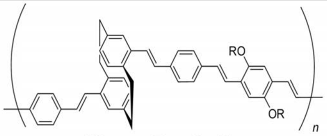
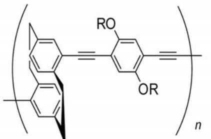
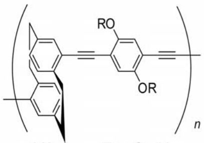
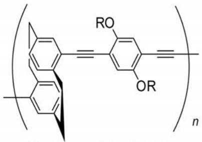
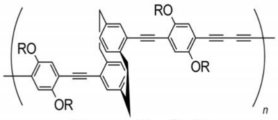
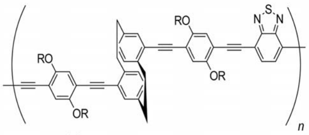
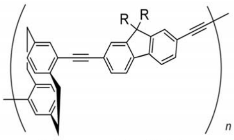
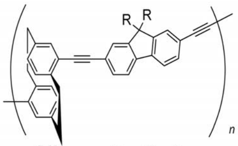
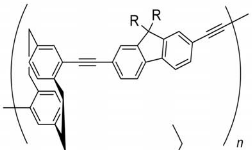
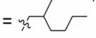
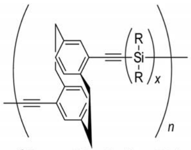
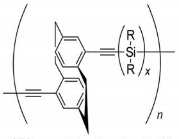
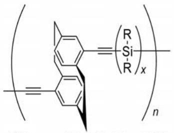
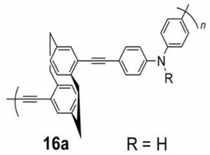
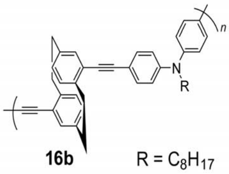
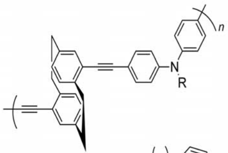
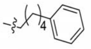
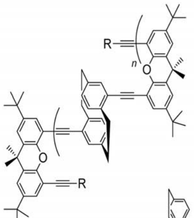
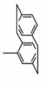
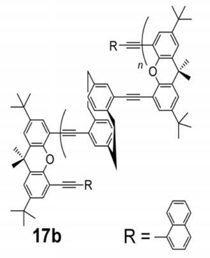
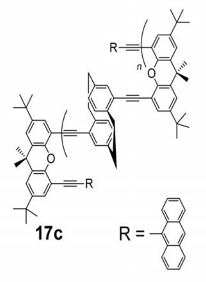
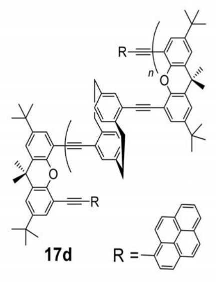
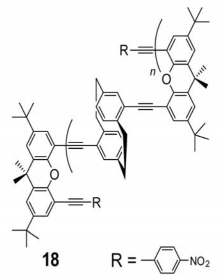
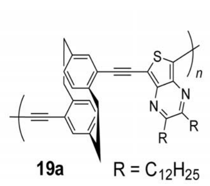
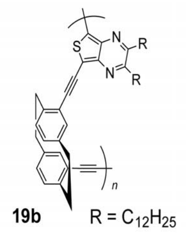
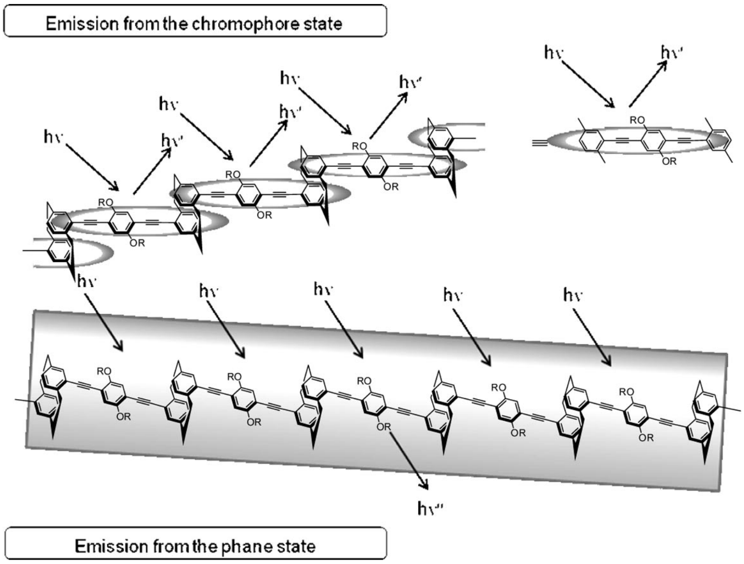
 **10a** R = C_6H_{13} λ_{max} (ex) = 398 nm λ_{max} (em) = 462 nm	 **10b** R = $C_{12}H_{25}$ λ_{max} (ex) = 397 nm λ_{max} (em) = 462 nm	 **10c** R = $C_{12}H_{25}$ λ_{max} (ex) = 423 nm λ_{max} (em) = 487 nm
 **11a** R = C_8H_{17} λ_{max} (ex) = 370 nm λ_{max} (em) = 501 nm	 **11b** R = $C_{12}H_{25}$ λ_{max} (ex) = 384 nm λ_{max} (em) = 517 nm	 **11c** R = $C_{16}H_{33}$ λ_{max} (ex) = 380 nm λ_{max} (em) = 505 nm
 **12** R = $C_{12}H_{25}$ λ_{max} (ex) = 406 nm λ_{max} (em) = 442 nm	 **13** R = $C_{12}H_{25}$ λ_{max} (ex) = 470 nm λ_{max} (em) = 565 nm	 **14a** R = C_6H_{13} λ_{max} (ex) = 372 nm λ_{max} (em) = 412 nm
 **14b** R = $C_{12}H_{25}$ λ_{max} (ex) = 370 nm λ_{max} (em) = 415 nm	 **14c** R =  λ_{max} (ex) = 371 nm λ_{max} (em) = 415 nm	 **15a** X = 2, R = CH_3 λ_{max} (ex) = 275 nm λ_{max} (em) = 385 nm
 **15b** X = 2, R = C_6H_{13} λ_{max} (ex) = 276 nm λ_{max} (em) = 384 nm	 **15c** X = 1, R = CH_3 λ_{max} (ex) = 271 nm λ_{max} (em) = 403 nm	 **16a** R = H λ_{max} (ex) = 360 nm λ_{max} (em) = 406 nm
 **16b** R = C_8H_{17} λ_{max} (ex) = 373 nm λ_{max} (em) = 410 nm	 **16c** R =  λ_{max} (ex) = 386 nm λ_{max} (em) = 416 nm	 **17a** R =  λ_{max} (ex) = 330 nm λ_{max} (em) = 410 nm

Table 2. *(continued)*.

 **17b** λ_{max} (ex) = 330 nm λ_{max} (em) = 397 nm	 **17c** λ_{max} (ex) = 340 nm λ_{max} (em) = 460 nm	 **17d** λ_{max} (ex) = 340 nm λ_{max} (em) = 430 nm
 **18** λ_{max} (ex) = 330 nm λ_{max} (em) = 410 nm	 **19a** λ_{max} (ex) = 470 nm λ_{max} (em) = 610 nm	 **19b** λ_{max} (ex) = 470 nm λ_{max} (em) = 610 nm



Scheme 5. Proposed emission mechanism of Chujo involving π-stacked pCp cores integrated into conjugated polymers.

[2.2]Paracyclophane as a Functional Unit in PPE and PPV Frameworks

The first reported pCp polymers were based on a PPV polymer backbone with a phenylene unit (**10a**–**c**) in the main chain.[25] Two intense absorbances at 340 and 398 nm, as well as a blue emission maximum at 462 nm for both **10a** and **10b**, were observed. The polymer **10c**, which contained an additional styryl unit at each terminus, exhibited an enhanced π-delocalization as evidenced by red shifts in both absorbance (λ = 362 and 423 nm) and fluorescence (λ = 487 nm).

Analogous PPE-based frameworks **11a**–**c** exhibited absorbance maxima at 370–385 nm.[26] The emissions were red-shifted relative to the PPV frameworks, as a strong green fluorescence at 510 nm was observed in **11a**–**c**. Installation of a diacetylene unit as a spacer between two phenylene units in structurally related **12** resulted in a red-shifted absorbance to 406 nm and a blue emission maximum at 442 nm.[27] The differences in absorbances were attributed to the effect of end-to-end chromophore length. In the PPE-based polymers, the conjugation length is larger owing to the longer alkene bonds, thus, resulting in a lower energy absorbance. In contrast, alkyne bonds are shorter with overall through-bond electron delocalization occurring over a shorter path. Owing to the shorter interchromophore distance within the PPE polymers, through space interactions are maximized with lower energy emission bands observed.

Installation of Donor or Acceptor Functionalities

Investigations of electron acceptor groups incorporated into a PPE-backbone led to benzodithiazole as a unit to facilitate electron delocalization within a pCp polymer.[28] Benzodithiazole has been used in conjugated polymers as an electron-accepting component and has successfully resulted in band gap reductions.[29] Polymer **13** displayed an absorbance maximum of 470 nm, which was attributed to a more efficient through-space delocalization and ICT between electron-accepting benzodithiazole and the electron-donating pCp. Additionally, **13** exhibited a strong orange emission at 565 nm.

Novel pCp-centered co-polymers containing fluorene units have also been studied.[30] Fluorene-based compounds are well known to exhibit efficient photo- and electroluminescent properties in the blue region.[31] The resulting PPE-based **14a**–**b** displayed absorbances centered at 370 nm, along with strong blue fluorescence at 415 nm. The alkyl-substituted fluorene unit acts as a donor and participates in ICT with the adjacent pCp core, resulting in the blue fluorescence.

After investigating the impact of fluorene units within the polymeric main chain, Chujo expanded to organosilicon moieties.[32] Organosilicon groups are of interest in semiconductor applications, as well as for photoresistors and non-linear optical (NLO) materials.[33] The resulting PPE polymers **15a**–**c** displayed a broad absorbance around 275 nm. A fluorescence maximum of 385 nm was observed for **15a** and **15b**, while **15c** showed a bathochromic emission at 403 nm. When phenylamine functionalities were integrated into a PPE-type structure,[34] the polymers **16a**–**c** exhibited a strong absorbance of 360 nm for the secondary amine, **16a** and up to 385 nm as the substitution on the amine increased in size. All the polymers exhibited a blue emission maximum around 410 nm, which resulted from ICT from the electron-donating amine unit towards the cyclophane core.

Xanthene has been recently incorporated into PPE-based scaffolds. The polymers **17a**–**d** exhibited strong absorbances and emissions, and in some cases, fluorescence resonance energy transfer (FRET) from the cyclophane moieties to the end-capping groups.[35] In particular, **17a**–**b** displayed an absorbance band at 330 nm, along with an emission up to 410 nm. **17a** and **17b** differ in structure, wherein an additional pCp or naphthalene was used as an end cap, respectively. When an anthracene unit was used as a capping agent in **17c**, a strong absorbance was observed at 340 nm, along with an emission at 460 nm. For **17c** there was a prominent overlap between the emission peak at 400 nm and the absorbance peak of 9-ethynylanthracene, which accounted for the FRET from the pCp core to the anthracene caps. When a larger pyrene system was used as an end-capping group in **17d**, an analogous absorbance was seen that also displayed a blue shift in emission at 430 nm. An additional xanthene co-polymer was prepared, wherein nitrobenzene was employed as an end-cap in **18**.[36] Polymer **18** exhibited an absorbance at 330 nm, as well as an additional, yet less intense, broad band at 370 nm. Nitro groups are electron-acceptors, which allows for more efficient electron transfer, and thus, lower energy absorbance. When **18** was excited at 333 nm, the molecule displayed an emission maximum at 410 nm.

To further investigate the impact of functional groups within the main chain of the pCp co-polymers, Chujo explored the influence of thieno[3,4-*b*]pyrazine. When pyrazine was used as a co-monomer in **19a**–**b**, an absorbance maximum at 470 nm was observed, along with an emission at 610 nm.[37] Thieno[3,4-*b*]pyrazine units possess a high degree of electron withdrawing character. The co-polymers **19a**–**b** displayed a resulting highly efficient ICT with the polymeric main chain consisting of a donor–acceptor–donor framework.

The studies by the Chujo group have resulted in the well-defined and characterized through-space conjugated and aromatic ring-layered polymers that contain pCp units in the main chain. The PPV- and PPE-based polymers display well-defined optical properties while also demonstrating that simple structural modification can result in tailored properties with sharp emissions that span from the blue region into the orange. Collectively, the studies have demonstrated the potential incorporation of pCp-based polymers in optoelectronic device, as well as single molecular wires and NLO materials.[38]

Bridge-Functionalized [2.2]Paracyclophane

Although attempts to control the optical properties of pCps have been based on deck substitution, our recent studies have resulted in the introduction of bridge-substituted pCp frameworks that display shifted fluorescence. A pCp was synthesized via a convergent approach wherein two dienes were assembled by a ditopic template to undergo a photocyclization in the solid state to produce a pCp core. In particular, we showed that co-crystallization of 4-benzylresorcinol (4-benz-res) with *p*-bis[2-(4-pyridyl)ethenyl]benzene (**bpep**) and subsequent double [2+2] photodimerization in the organic solid state results in the stereospecific formation of *rctt*-tetrakis(4-pyridyl-cyclobutyl)[2.2]paracyclophane (**20**) (Figure 3) mediated by O–H···N hydrogen bonds.[39] Consistent with Schmidt's topochemical postulate,[40] the photoreaction is achieved owing to the olefins being aligned parallel and separated at a distance of less than 4.2 Å. The photoreaction afforded **20** quantitatively with the crystal packing environment prohibiting a [2+2] cycloaddition from occurring between adjacent hydrogen-bonded structures (Figure 3).

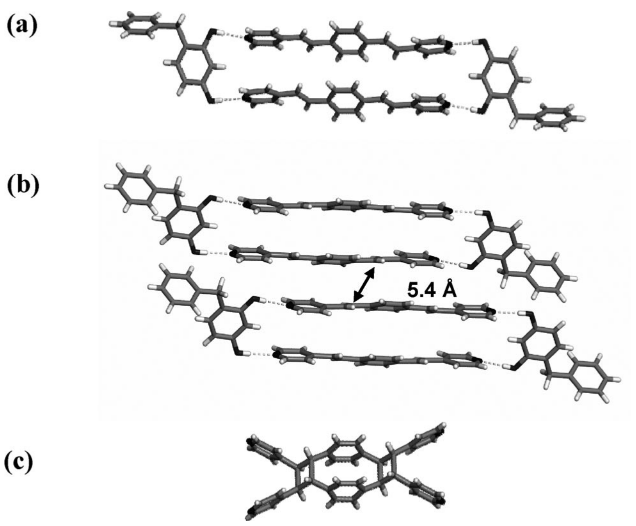
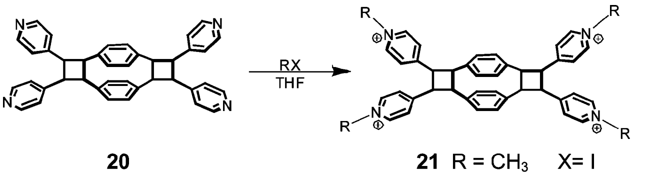


Figure 3. Crystal structure of (a) discrete assembly (**bpep**)·(4-benz-res), (b) adjacent assemblies, and (c) pCp **20**.

A comparison of the emission spectrum of **20** with pCp revealed a large bathochromic shift from 356 nm to 414 nm despite the presence of the saturated cyclobutane groups that can be expected to prohibit interchromophore communication in the absence of conjugation.[41] In addition, **20** exhibited a relative red shift in fluorescence compared to the parent diene chromophore (401 nm).[42] The red-shifted emission corresponded to a longer wavelength excitation at 380 nm.[41] From our observations, we concluded that the cyclobutanes likely acted as efficient through-bond donors that facilitate nonconventional ICT outward from the cyclobutyl-pCp core to the distal charged and electron-poor pyridine groups. Indeed, the strained nature of the core would be expected to lead to an efficient electron-donating scaffold.

Importantly, previous studies into bridge-substituted pCps that target the aliphatic bridges had been mostly limited to benzylic halogenations at the bridges,[43] as well as ring annulations.[44] Prior to our studies, Hasegawa and coworkers had also reported a solid-state synthesis of a pCp with bridge substituents. In contrast to our template method, however, the synthesis relied on fortuitous effects of crystal packing to enable the olefins to be in position for the double cycloaddition.[45] Optical properties of the pCp were not a main focus.

In addition to the parent pCp **20**, we studied optical effects of N-alkylation (Scheme 6).[41] Tetracationic **21** and **22**, achieved in a post-synthetic modification of **20**, revealed large bathochromic shifts in absorbance and emission upon alkylation (Figure 4). Absorbance maxima were shifted to 422 and 427 nm for **21** and **22**, respectively. Excitation of the pCps at 380 nm resulted in a broad emission peak centered at 493 nm. The quaternization of the pyridyl N-atoms, thus, allowed for a strong polarization over the entire pCp core by increasing electron withdrawing properties of the distal pyridines. A polarization of charge was supported by density functional theory (DFT) calculations. The alkylation, effectively, enhanced a nonconventional ICT owing to an ability of the pyridinium substituents to withdraw electron density from the pCp fluorophore via the strained cyclobutane bridges.



20

21 R = CH_3 X= I
22 R = CH_2CH_3 X = I

Scheme 6. Synthesis of tetracationic pCp **21** and **22**.

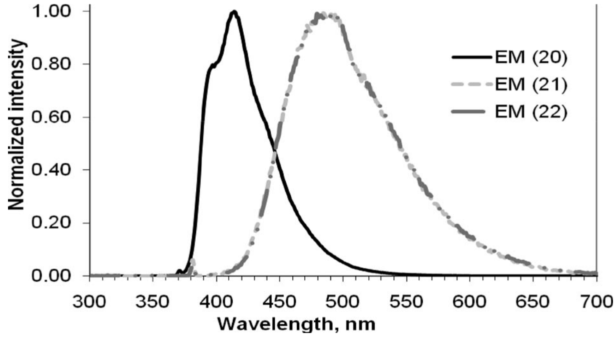


Figure 4. Emission spectra of **21** and **22** compared to **20**.

Conclusions

Our review has focused on the synthesis and optical properties of pCp and derivatives. Owing to the extensive work on the properties of pCp-based molecules and polymers, pCp has further developed beyond "bent and battered benzene rings" of interest to hydrocarbon chemists. The integration of pCp in materials science has resulted in an understanding of photophysical properties that result from a unique structure and has provided a foundation to harness properties of the framework. Both molecules and polymers have involved tailoring of properties of the pCp core via incorporation of electron-donating and/or -withdrawing groups. We have also demonstrated that through our related work on the solid-state synthesis of a bridge-substituted pCp, nonconventional ICT can be achieved in a strained and saturated system. Continued efforts to design unique pCp-based molecules and polymers are expected to lead to an incorporation of the stacked framework as a basis in emerging fluorophoric devices and optoelectronic technologies.[12,37]

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