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COMMUNICATION

Organic nanocrystals of [2.2]paracyclophanes achieved *via* sonochemistry: enhanced and red-shifted emission involving edge-to-face chromophores†

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We have prepared organic nanocrystals of [2.2]paracyclophane (pCp) and tetrakis(4-pyridylcyclobutyl)[2.2]paracyclophane (tpcp) *via* sonochemistry. Both nanocrystals exhibit an enhanced fluorescence compared to dilute solution, while the tpcp nanocrystals also demonstrate a red-shifted fluorescence.

Introduction

Over the past decade, extensive research has been conducted on the controllable synthesis of nanocrystals[1] owing to correlations between size,[2] morphology,[3] and optoelectronic properties.[4] Inorganic and polymer-based nanocrystals have garnered much interest, owing to emerging widespread applications in fields ranging from diagnostic medicine[5] to materials science.[6] Organic nanocrystals of small molecules remain relatively less studied despite a potential to modify the structures and tune optical properties of such solids[7] using methods of organic synthesis.

Early studies on the fluorescence of organic nanomaterials based on small molecules were conducted by Nakanishi[8] and Yao,[9] which involved aromatics such as perylene, phthalocyanine, and pyrazoline. More recent studies by Park,[10] Diau,[11] and Yang[12] have focused on conjugated stilbenoids that exhibit strong emission, yet are weakly fluorescent in solution. Enhancements of solid-state fluorescence are quite unusual with organic materials owing to facile quenching of chromophores[13] in the condensed phase, with conjugated systems such as poly(*p*-phenyleneethynylenes),[14] pseudoisocyanines,[15] and pentaphenylsilols[16] being exceptions.

With this in mind, we report here the sonochemical preparation[17] of nanocrystals of [2.2]paracyclophane (pCp) and the laterally- substituted derivative tetrakis(4-pyridylcyclobutyl)[2.2]paracyclophane (tpcp) (Fig. 1).[18] Originally studied by Cram,[19] and extensively developed by Hopf[20] and others,[21] pCp has garnered much interest owing to unique properties[21] (*e.g.* optical, reactivity, chirality) conferred by the two co-facially stacked benzene rings connected by aliphatic bridges. Moreover, while both synthesis and materials aspects of pCp are of much continued interest, the generation of nanostructured pCp is underdeveloped. We demonstrate that while exclusive reprecipitation does not afford nanostructured pCp, the use of sonochemistry produces nanocrystals of sizes <500 nm. Nanodispersions of the pCps are also shown to exhibit enhanced emission compared to solution. The emission is attributed to edge-to-face aggregation and packing in the solid state that promotes intermolecular interactions able to maximize interchromophore communication (Scheme 1).[22]

Results and discussion

Our initial attempts to generate nanocrystals of pCp involved the reprecipitation method wherein pCp is dissolved in a hot polar solvent, which is followed by rapid injection into an antisolvent. pCp (0.15 g) was, thus, dissolved in toluene (7.0 mL) and rapidly injected into ethanol (100 mL). The resulting solid was analyzed using powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM). SEM micrographs revealed large well-defined crystals of micrometer-sized dimensions, wherein the smallest crystals were on the order of 5 μm in both length and width (Fig. 2a,b). The resulting microcrystals displayed block morphologies and were agglomerated as stacked crystals. An inspection of a PXRD pattern confirmed the solid to match the reported

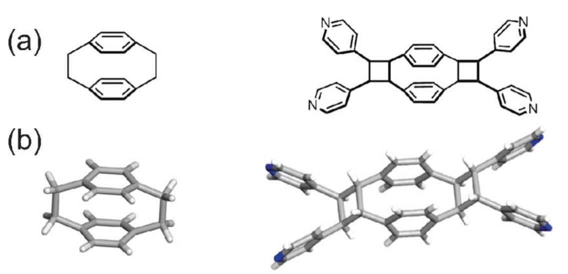

Fig. 1 pCp and tpcp: (a) schematics and (b) X-ray crystal structures.

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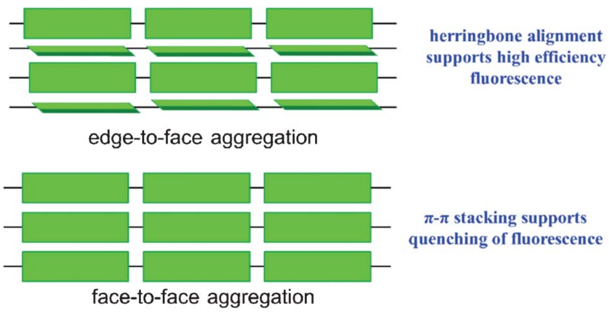
† Electronic Supplementary Information (ESI) available: Excitation and emission spectra, PXRD characterization, and SEM micrographs. See DOI: 10.1039/c2ce26000j



Scheme 1 Solid-state packing motifs that influence emission.

structure of pCp,[23] which was evidenced by prominent peaks at 2θ = 15.0°, 16.1°, 25.9°, and 27.7° (Fig. 2c).

To form nanocrystals of pCp, we turned to a sonochemical approach. The method has been shown to generate crystals of nanoscale dimensions wherein more standard reprecipitation[24] fails.[25] In our experiments, low-intensity ultrasonic radiation using a sonication cleaning bath was applied in crystal growth of pCp. In a typical experiment, pCp (0.15 g) was dissolved in DMF (3.0 mL) and rapidly injected into water (100 mL) subjected to ultrasonic radiation. After 5 min of sonication, the suspension was vacuum filtered through an 8 μm membrane filter (Whatman) and analyzed using PXRD. The resulting diffractogram revealed the structure of the solid generated using sonochemistry to match pure pCp (Fig. 3).

SEM analysis of the solid obtained *via* sonochemistry confirmed the generation of nanometer-sized crystals of pCp. The crystals exhibited a spherical, or approximate cube, morphology,[26] with the smallest crystals displaying lengths and widths that range from 200 to 500 nm (Fig. 4a,b). An aliquot of the original suspension generated using the sonochemistry was analyzed using dynamic light scattering (DLS). DLS measurements revealed average particle sizes of *ca.* 477 nm with a polydispersity index (PDI) of 0.146 (Fig. 4c).

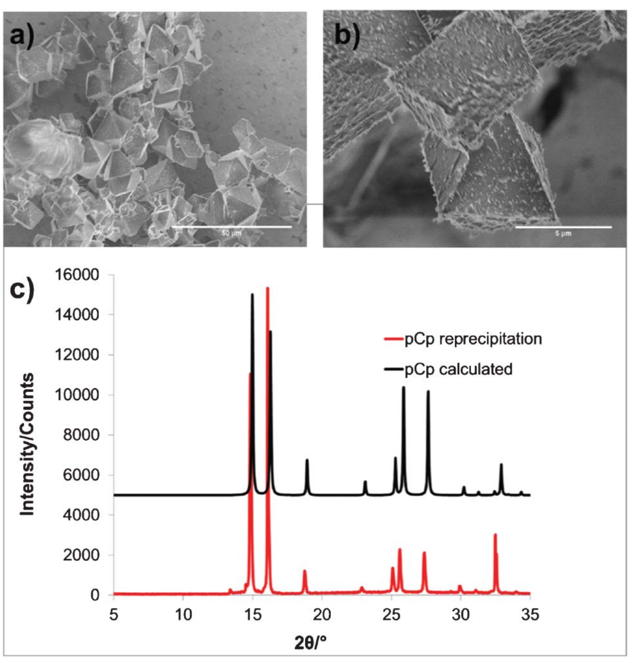


Fig. 2 (a,b) SEM micrographs of microcrystals of pCp from reprecipitation and (c) PXRD diffractogram compared to calculated powder pattern of pCp.

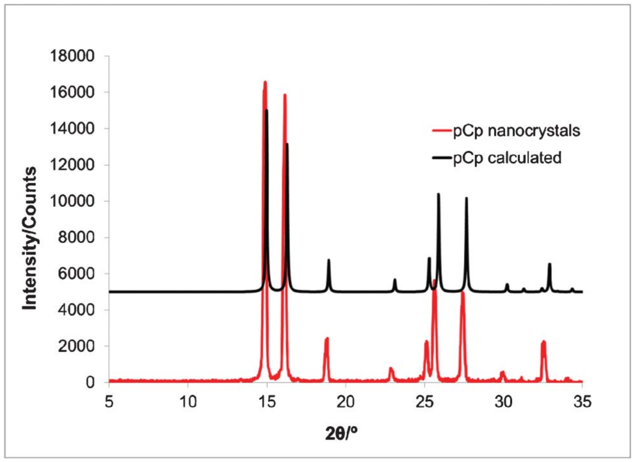


Fig. 3 PXRD diffractogram of pCp treated with sonochemistry compared to calculated pattern of pure pCp.

We next turned to influences of surfactant on nanocrystal formation. The introduction of a surfactant to generate nanomaterials can promote a decrease in particle size *via* the formation of micelles, where increases in nucleation rate are also realized.[27] Smaller particles could, thus, be expected in the presence of a surfactant.

Anionic sodium dodecyl sulfate (SDS) was employed as the surfactant, with water as antisolvent. In the experiment, pCp (0.15 g) was dissolved in DMF (3.0 mL) and rapidly injected into 0.021 M aqueous SDS (100 mL) subjected to ultrasonic radiation for 5 min. Following vacuum filtration through an 8 μm filter, the solid was analyzed using PXRD and SEM, while an aliquot of the suspension was analyzed using DLS. SEM micrographs demonstrated the formation of approximately spherical particles that range from 100 to 400 nm in diameter (Fig. 5a,b). DLS measurements demonstrated particles with sizes of *ca.* 340 and a PDI of 0.270. The incorporation of the SDS, thus, resulted in a decrease in particle size of nanocrystalline pCp (Fig. 5c).

With the successful formation of nanocrystals of pCp achieved, we extended our efforts to the laterally-substituted derivative tpcp. The pCp is achieved *via* a double [2 + 2] photodimerization conducted in the solid state.[18,28] Tpcp was, thus, dissolved in hot

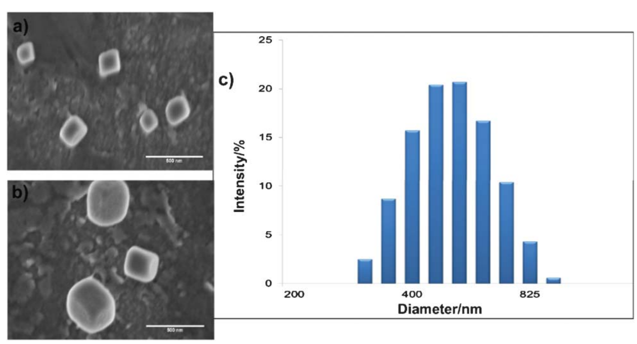


Fig. 4 (a, b) SEM micrographs of pCp nanocrystals generated using sonochemistry and (c) particle size distribution.

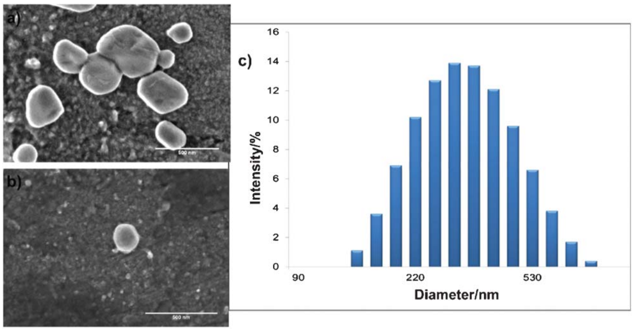


Fig. 5 (a,b) SEM micrographs of pCp nanocrystals prepared using sonochemistry with the addition of SDS and (c) particle size distribution.

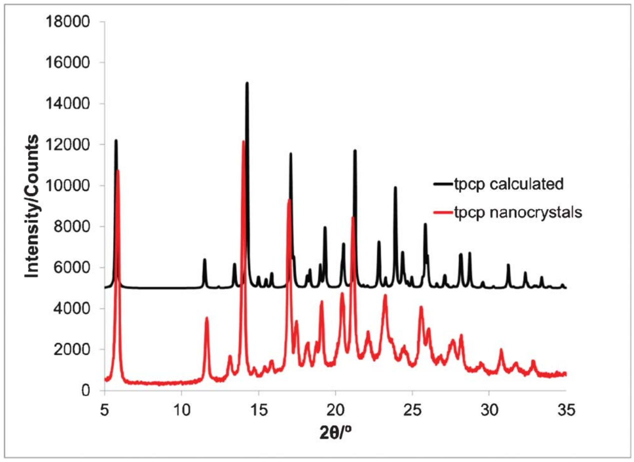


Fig. 7 PXRD diffractogram of tpcp nanocrystals compared to the calculated powder pattern.

DMF and rapidly injected into water. Similar to initial experiments involving pCp, SEM micrographs revealed large crystals of tpcp of rectangular morphology with lengths and widths of 15 μm and 4 μm, respectively (Fig. 6a,b). PXRD (Fig. 6c) confirmed the solid precipitate as pure crystalline tpcp.[29]

Sonochemistry was next applied to promote the generation of nanocrystals of tpcp. Tpcp (0.05 g) was dissolved in hot DMF (0.7 mL) and rapidly injected into water (100 mL) subjected to ultrasonic radiation. After 5 min of sonication, the suspension was filtered through an 8 μm membrane filter and analyzed using PXRD and SEM. An analysis of the PXRD pattern supported the solid generated using sonochemistry to match tpcp (Fig. 7).

SEM analysis revealed the formation of tpcp nanocrystals. The smallest particles were spherical in shape, displaying sizes of *ca.* 250 nm (Fig. 8a,b). Moreover, when SDS was used as surfactant, particles on the order of 50 nm readily formed (Fig. 8c,d). Thus, the incorporation of SDS resulted in an effective five-fold decrease in particle size. DLS measurements were notably inconclusive owing to rapid settling of the nanoparticles.[30] Indeed, a ζ-potential of −2.5 mV was determined, which is consistent with aggregation of the small particles within the dispersion.[30]

Optical properties of nanosized pCp and tpcp were investigated. Samples of pCp and tpcp obtained from the sonochemistry experiments were each examined as nanocrystalline suspensions in either water or aqueous solutions of SDS[31] and compared to dilute solutions of the same concentration. As reported, tpcp displays red-shifted excitation and emission in solution compared to pCp. The red-shift occurs despite a lack of continuous p-orbital conjugation. The fluorescence was attributed to the cyclobutane rings acting as efficient electron donors that promote internal charge transfer within the π-stacked molecule.[28]

From our experiments, both pCp and tpcp were determined to exhibit more intense fluorescence as nanocrystal suspensions compared to dilute solution. While nanocrystalline pCp exhibited the same emission wavelength (356 nm) as pCp in solution, the nanoparticles without and in the presence of SDS displayed fluorescence *ca.* 40 times more intense (Fig. S-18†). For tpcp, the nanocrystals were *ca.* 17 times more intense than dilute solution. In contrast to pCp, the nanoparticles of tpcp also exhibited a bathochromic emission at 490 nm in the presence of the SDS (Fig. 9). The shift can likely be attributed to appreciable hydrogen

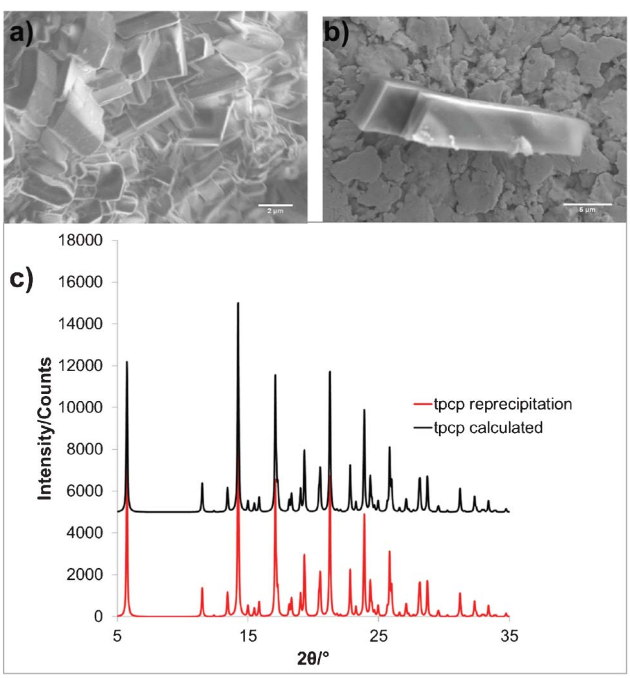


Fig. 6 (a,b) SEM micrographs of tpcp collected from reprecipitation and (c) PXRD diffractogram compared to the calculated powder pattern.

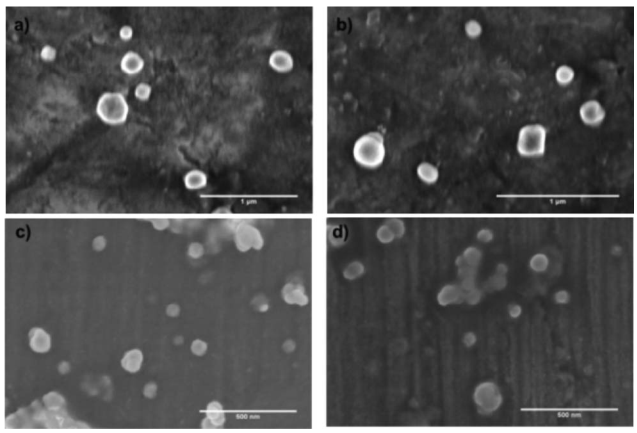


Fig. 8 Nanocrystals of tpcp nanocrystals using (a,b) sonochemistry and (c,d) sonochemistry with SDS.

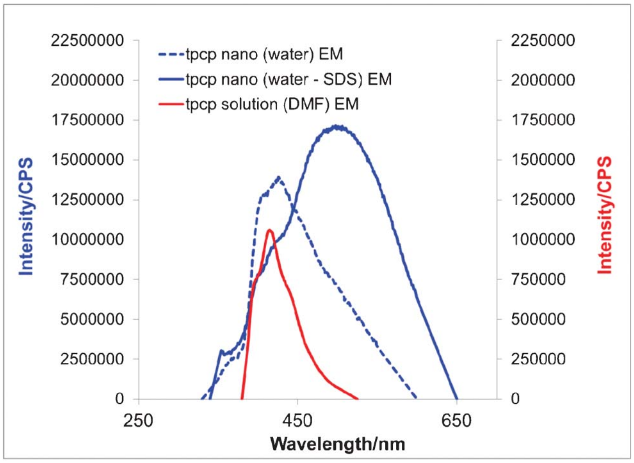


Fig. 9 Emission of tpcp nanocrystals compared to dilute solution (nanoparticles on primary axis and solution on secondary axis).

bonding of water molecules associated with SDS at the N-atoms of the pyridyl groups.[32] The presence of hydrogen bonds may also account for the significant decrease in particle size when both sonochemistry and SDS were used to produce the nanocrystals. A similar red shift has been observed for N-alkylated tpcp.[28] We also note that microsized crystals of pCp and tpcp exhibited fluorescence more intense than solution yet significantly less (*i.e. ca.* 10 times less) than the nanocrystal suspension. The enhance fluorescence of the nanoparticles compared to the microsized crystals may be related to surface effects and/or aggregation of the nanoparticles.[33] The microcrystals of tpcp in the presence of SDS, in contrast to the nanocrystals, also did not exhibit an appreciable red shift in fluorescence (Fig. S-19†). The lack of a red shift is also supportive of influences of hydrogen bonding being appreciable along the surfaces of the nanocrystals.

The enhanced fluorescence of nanocrystalline pCp and tpcp, as well as the related microcrystals, compared to solution can be attributed to aggregation that is maintained in the solid and arises from minimal intermolecular π-overlap of the stacked π-faces.[34] Fluorescence of organic chromophores is typically quenched by either by co-planarization at the molecular level[35] or intermolecular aggregation at the supramolecular level.[36] Given that pCp and tpcp possess two benzene rings covalently enforced in a face-to-face geometry, forces between molecules are expected to significantly impact fluorescence in the solid, owing to less conformational freedom within the crystal. Both pCp[23] and tpcp[29] assemble edge-to-face, or in a herringbone fashion, in the crystalline state (Fig. 10), which is a geometry known to support enhanced fluorescence.[37] Combinations of multiple hydrogen-bonding also support the edge-to-face geometries (*e.g.* C–H···π, C–H···N forces) by increasing conformational rigidity, as particularly in the case of tpcp. For the nanocrystalline suspensions, the edge-to-face aggregation and rigid stacking is presumably maintained in the condensed environment.[38]

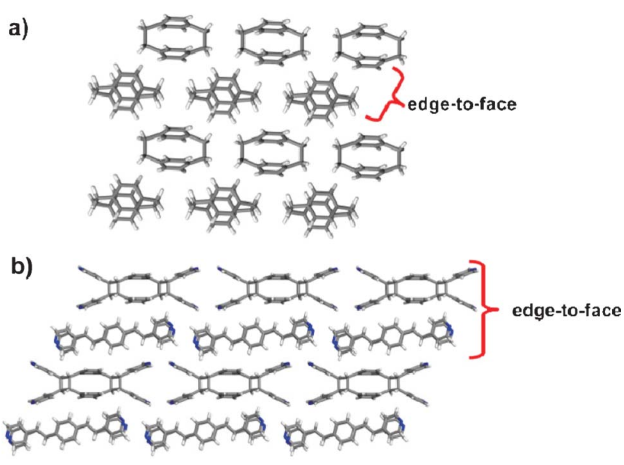


Fig. 10 Edge-to-face packing of crystalline: (a) pCp and (b) tpcp.

Conclusion

In this report, we have described a sonochemical approach to prepare nanostructured pCps. The nanocrystals are on the order of 100–500 nm and exhibit optical properties that differ compared to solution. Both nanostructured pCp and tpcp display more intense fluorescence, which is ascribed to edge-to-face packing being maintained in the nanocrystalline solid. We are currently focused on preparing nanocrystals of additional pCps, where herringbone stacking of the chromophores may also be preferred.

Experimental

Materials and instruments

pCp was purchased from Carbosynth (Compton, Berkshire, UK). SDS was purchased from Sigma Aldrich Chemical Company (St. Louis, MO, USA). N.N-dimethylformamide, toluene, and ethanol were purchased from Fisher Scientific Company (Pittsburgh, PA, USA). tpcp was prepared as reported.[18a] All chemicals were used without further purification. PXRD data was collected using a Bruker D-5000 diffractometer equipped with a Bruker SOL-X energy-sensitive detector using Cu-Kα radiation (λ = 1.54056 Å). Particle size measurements were determined by a Zetasizer Nano ZS (Malvern, Southborough, MA) instrument at 25 °C. The reported particle size and PDI values are averages of three measurements. SEM images were obtained using a Hitachi S-4800 with an accelerating voltage range of 2–5 kV. SEM samples were prepared by depositing each sample on a Si wafer. Absorption and emission measurements were obtained using a HORIBA Jobin Yvon FluoroMax-4 (Edison, NJ, USA). All measurements were made on the as-prepared suspensions with a scan rate of 5 mm sec^{-1} and both slit widths set to 2 nm.

pCp nanocrystal synthesis. Nanocrystals of pCp were prepared by dissolving 150 mg of pCp in 5 mL of DMF. The solution was rapidly injected into 100 mL of distilled water at ambient temperature and sonicated for 5 mins in a cleaning bath (Branson 2510*R*-DTM). After sonication, the sample was filtered through an 8 μm membrane filter (Whatman Grade 2) and dried. The surfactant crystallization was performed with 0.021 M SDS as antisolvent.

tpcp nanocrystal synthesis. Nanocrystals of tpcp were prepared by dissolving 50 mg of pcp in 0.7 mL of DMF. The solution was rapidly injected into 100 mL of distilled water at ambient temperature and sonicated for 5 mins in a cleaning bath (Branson 2510*R*-DTM). After sonication, the sample was filtered through an 8 μm membrane filter (Whatman Grade 2) and dried.

The surfactant crystallization was performed with 0.021 M SDS as the antisolvent.

Acknowledgements

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