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

Elizabeth Elacqua,a Paul T. Jurgens,a Jonas Baltrusaitis,a,c and Leonard R. MacGillivray*a,b

a  Department of Chemistry, University of Iowa, Iowa City, IA 52242
b  Optical Science and Technology Center, University of Iowa, Iowa City, IA 52242
c  Central Microscopy Research Facility, University of Iowa, Iowa City, IA 52242
len-macgillivray@uiowa.edu

Supporting Information

Materials: 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. All chemicals were used without further purification.

Methods: PXRD data was collected using a Bruker D-5000 diffractometer equipped with a Bruker SOL-X energy-sensitive detector using CuKα radiation (λ = 1.54056 Å). Particle size measurements were determined by a Zetasizer Nano ZS (Malvern, Southborough, MA) instrument at 25°C. SEM images were obtained using a Hitachi S-48000 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. Solution-based measurements were obtained using N,N-dimethylformamide as solvent. Micrometer-sized and Nanometer-sized particles were measured as suspensions in water and 0.021 M SDS(aq). The suspension measurements were conducted using an aliquot of the suspension after re-precipitation (micro) and/or after sonication (nano).
PXRDs

Figure S-1: PXRD diffractogram of a sample obtained during reprecipitation of pCp compared to the calculated pattern.

Figure S-2: PXRD diffractogram of pCp nanocrystals compared to the calculated pattern.
Figure S-3: PXRD diffractogram of a sample obtained during reprecipitation of tpcp compared to the calculated pattern.

Figure S-4: PXRD diffractogram of tpcp nanocrystals compared to the calculated pattern.
Spectroscopic Data

Figure S-5: Excitation spectrum of pCp in DMF.

Figure S-6: Excitation spectrum of tpcp in DMF.
Figure S-7: Excitation spectra of pCp microcrystalline suspensions.

Figure S-8: Excitation spectra of tpcp microcrystalline suspensions.
Figure S-9: Excitation spectra of pCp nanocrystalline suspensions.

Figure S-10: Excitation spectra of tpcp nanocrystalline suspensions.
Figure S-11: Emission spectrum of pCp in solution.

Figure S-12: Emission spectrum of tpcp in solution.
Figure S-13: Emission spectra of pCp microcrystalline suspensions.

Figure S-14: Emission spectra of tpcp microcrystalline suspensions.
**Figure S-15:** Emission spectra of pCp nanocrystalline suspensions.

**Figure S-16:** Emission spectra of tpcp nanocrystalline suspensions.
Comparison of Emission Profiles

**Figure S-17:** Emission spectra of pCp microcrystalline suspensions compared to pCp in solution (solution result is plotted on the secondary axis).
Figure S-18: Emission spectra of pCp nanocrystalline suspensions compared to pCp in solution (solution result is plotted on the secondary axis).
Figure S-19: Emission spectra of tpcp microcrystalline suspensions compared to tpcp in solution (solution result is plotted on the secondary axis).
Figure S-20: Emission spectra of tpcp nanocrystalline suspensions compared to tpcp in solution (solution result is plotted on the secondary axis).
SEM Micrographs:

**Figure S-21:** SEM micrographs of pCp microcrystals from reprecipitation.

**Figure S-22:** SEM micrographs of pCp nanocrystals generated using sonochemistry.
Figure S-23: SEM micrographs of pCp nanocrystals generated using sonochemistry with the addition of SDS.

Figure S-24: SEM micrographs of tcep microcrystals from reprecipitation.
**Figure S-25:** SEM micrographs of tpcp nanocrystals generated using sonochemistry.

**Figure S-26:** SEM micrographs of tpcp nanocrystals generated using sonochemistry with the addition of SDS.