## Supporting information for

## Aggregation-Free Sensitizer Dispersion in Rigid Ionic Crystals for Efficient Solid-State Photon Upconversion and Demonstration of Defect Effects

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Figure S1. FT-IR spectra of ADCA (blue) and DCA<sub>2</sub>ADC (green) powder samples.



**Figure S2.** Photoluminescence decays of (DCA)<sub>2</sub>ADC in 10  $\mu$ M MeOH solution (blue) and solid crystals (green). The excitation wavelength was selected as  $\lambda_{ex}$  = 365 nm and decays were obtained at 440 nm. Fitting lines are indicated by red lines.

	(DCA) <sub>2</sub> ADC crystals	PdMesoP-(DCA)2ADC crystals
Crystal system	Monoclinic	Monoclinic
Space group	P21/c	P21/c
a (□)	9.7956(7)	9.807(3)
b ( 🗆 )	17.7834(15)	17.777(5)
$c(\Box)$	10.0007(8)	10.025(3)
$\alpha$ ( $\Box$ )	90	90
$\beta$ ( $\Box$ )	99.394(3)	99.418(3)
$\gamma(\Box)$	90	90
Final R indices	0.0492	0.0446

Table S1. Cell parameters of (DCA)<sub>2</sub>ADC crystals and PdMesoP-(DCA)<sub>2</sub>ADC crystals



**Figure S3.** Photoluminescence decays of  $(DCA)_2ADC$  crystals (green) and PdMesoP- $(DCA)_2ADC$  crystals (purple). The excitation wavelength was selected as  $\lambda_{ex}$  = 365 nm and decays were obtained at 440 nm. Fitting lines are indicated by red lines.



**Figure S4.** UV-vis absorption spectra of PtOEP-(DCA)<sub>2</sub>ADC crystals (purple), diluted THF solution of PtOEP (10 µM, blue) and bulk PtOEP solid (red).



**Figure S5.** Double logarithmic plots of the UC PL intensity of PdMesoP-(DCA)<sub>2</sub>ADC crystals as a function of the excitation intensity. Linear fits with slope 2 and 1 in the lower and higher excitation intensity regimes are shown.



**Figure S6.** A PXRD pattern of PdMesoP-(DCA)<sub>2</sub>ADC powder (green) and a simulated pattern of (DCA)<sub>2</sub>ADC from its single crystal structure measured (gray).



Figure S7. SEM image of PdMesoP-(DCA)<sub>2</sub>ADC ground powder.



**Figure S8.** UV-vis absorption spectra (solid lines) and emission spectra (broken lines) of single crystals (red) and ground powder (green) of PdMesoP-(DCA)<sub>2</sub>ADC. The excitation wavelength was selected as  $\lambda_{ex}$  =365 nm.



**Figure S9.** Photoluminescence spectra of PdMesoP-(DCA)<sub>2</sub>ADC ground powder prepared under Ar atmosphere with various excitation intensities ( $\lambda_{ex}$  = 532 nm). The scattered incident light was removed by using a 532 nm notch filter.



**Figure S10.** Photoluminescence decays at 435 nm for (a) single crystals and (b) ground powder of PdMesoP-(DCA)<sub>2</sub>ADC. The blue fitting curves were obtained by considering the equation (2) in the main text. Insets show magnifications at faster decay range.