Supporting Information for

A Panchromatic Hybrid Crystal of Iodoplumbate Nanowires and *J*-aggregated Naphthalene Diimides with Long-lived Charge-separated States

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1. Experimental Details and Synthesis

Materials and Methods: *N*-methylpyrrolidin-2-one (NMP, analytical reagent grade), PbI_2, hydroiodic acid (55%, w/w), ethanol (analytical reagent grade) were obtained from commercial suppliers. All chemicals and reagents were used as received unless otherwise stated. NMR spectra were recorded with a Bruker Avance III 500 MHz NMR spectrometer. ESI mass spectra were recorded on a LCQ Fleet from Thermo Fisher Scientific. IR spectra were recorded in the range 4000-400 cm^{-1} on a Perkin-Elmer FT-IR spectrum 2000 spectrometer with pressed KBr pellets. The electron spin resonance (ESR) measurements were recorded on a Bruker A300 instrument operating in the X-band at room temperature. Powder X-ray diffraction (PXRD) patterns were recorded with a Rigaku MiniFlex-II X-Ray diffractometer with Cu Kα radiation (λ = 1.54178 Å). TGA measurements were performed on a TG-209 system with a heating rate of 10 °C/min under an N_2-atmosphere. UV-Vis diffuse reflectance spectra were recorded at room temperature on a Varian Cary 500 UV-Vis spectrophotometer equipped with an integrating sphere.

Synthesis of DPNDI: The organic ligand *N*,*N*'-di(4-pyridyl)-1,4,5,8-naphthalene diimide (DPNDI) was synthesized following the reported process.[S1] ^1H NMR (500 MHz, CF_3COOD, 298K): δ = 9.12 (d, *J* = 7 Hz, 4H), 9.05 (s, 4H), 8.38 (d, *J* = 7 Hz, 4H). ESI-MS *m/z*: Calculated for $C_{24}H_{12}N_4O_4$: 420.09, Found: 420.09.

Synthesis of (H_2DPNDI)·(2I): A solution (5 mL) of EtOH was carefully layered on a NMP (5 mL) solution of DPNDI (0.10 mmol, 0.042g), and 0.5 mL HI (55%, w/w). Red block crystals of complex **(H_2DPNDI)·(2I)** were obtained after several days (*ca.* 65% yield based on DPNDI).

Synthesis of (Et_2DPNDI)·(2I): Iodoethane (3.12 g, 20 mmol) was added to a 1:1 mixture of MeCN/DMF (30 mL) in a round-bottomed three-necked flask, and then the DPNDI (2.10 g, 5 mmol) was added in the solution. After heating under reflux for 8 h, the reaction mixture was cooled to room temperature, and the precipitate was collected by filtration and washed with CH_2Cl_2. (*ca.* 86% yield based on DPNDI). The solid was dissolved in MeCN/H_2O (1/2, v/v), the filtrate was allowed to stand at room temperature, red block crystals of **(Et_2DPNDI)·(2I)** were obtained within two days.

Synthesis of complex 1. A solution (5 mL) of EtOH was carefully layered on a NMP (5 mL) solution of DPNDI (0.03 mmol, 0.013g), PbI_2, (0.09 mmol, 0.042 g) and 0.2 mL HI (55%, w/w). Black block crystals of complex **1** were obtained after several days (*ca.* 21% yield based on DPNDI). IR data (KBr, cm^{-1}): 3425(m), 3047(w), 2968(w), 2897(m), 1697(m), 1635(s), 1537(m), 1363(s), 1287(m), 1209(m), 1124(w), 1086(w), 982(w), 885(w), 756(m), 662(m), 536(w).

2. Single Crystal X-ray Diffraction Analysis

2.1. Methods and crystal data

Suitable single crystal of complex **1,** $(H_2DPNDI)\cdot(2I)$ and $(Et_2DPNDI)\cdot(2I)$ were mounted on glass fiber for the X-ray measurement. Diffraction data were collected on a Rigaku-AFC7 equipped with a Rigaku Saturn CCD area-detector system. The measurement was made by using graphic monochromatic Mo Kα radiation (λ= 0.71073 Å) at 293 K under a cold nitrogen stream. The frame data were integrated and absorption correction using a Rigaku *CrystalClear* program package. All calculations were performed with the *SHELXTL-97* program package [S2], and structures were solved by direct methods and refined by full-matrix least-squares against F^2. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms except for the water molecules. The H atoms of water were located in difference Fourier maps and their positions were refined with O-H bond-length restraints of 0.84 Å. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 1024096, 1038297 and 1038298 for complex **1,** $(H_2DPNDI)\cdot(2I)$ and $(Et_2DPNDI)\cdot(2I)$, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal Data and Structure Refinements for **1,** $(H_2DPNDI)\cdot(2I)$ and $(Et_2DPNDI)\cdot(2I)$.

Complex	1	$(H_2DPNDI)\cdot(2I)$	$(Et_2DPNDI)\cdot(2I)$
Crystal size (mm)	0.34×0.27×0.14	0.40×0.18×0.15	0.34×0.22×0.15
Empirical Formula	$C_{58}H_{50}I_{12}N_{10}O_{12}Pb_4$	$C_{24}H_{16}I_2N_4O_5$	$C_{28}H_{22}I_2N_4O_4$
Formula weight	3430.64	694.21	732.30
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	*C*2/*c*	*P*2/*c*
***a* (Å)**	11.361(2)	15.786(3)	12.006(2)
***b* (Å)**	13.250(3)	8.5029(17)	7.4721(15)
***c* (Å)**	15.572(3)	17.617(4)	16.822(6)
***α* (°)**	66.81(3)	90.00	90.00
***β* (°)**	78.10(3)	102.38(3)	117.21(2)
***γ* (°)**	74.92(3)	90.00	90.00
***V* (Å^3)**	2066.4(7)	2309.6(8)	1342.1(6)
Z	1	4	2
***Dc* (g/ cm^3)**	2.757	1.996	1.812
μ(Mo Kα) (mm^{-1})	12.662	2.769	2.385
***F*(000)**	1528	1336	712
Collected reflections	19971	9225	12197
Independent reflections	9307 (0. 0378)	2651	3064
Goodness-of-fit on F^2	1.038	1.179	1.074
$R_1{}^a$, $wR_2{}^b$ ($I>2\sigma(I)$)	0.0404, 0.0933	0.0305, 0.0749	0.0535, 0.1329
$R_1{}^a$, $wR_2{}^b$ (all data)	0.0599, 0.1059	0.0319, 0.0757	0.0606, 0.1386

Table S2. Hydrogen Bonds for complex **1**.

D-H/A	D-H (Å)	H...A (Å)	D...A (Å)	<D-H/A (deg)	symmetry
O6-H32B...O4	0.841(10)	2.14(7)	2.852(9)	143(9)	-x+2, -y+1, -z+1
N1-H1...O5	0.86	1.93	2.729(12)	153.7	-x+1, -y+3, -z
N3-H3A...O6	0.86	1.83	2.673(10)	167.8	–

2.2. Crystal structure

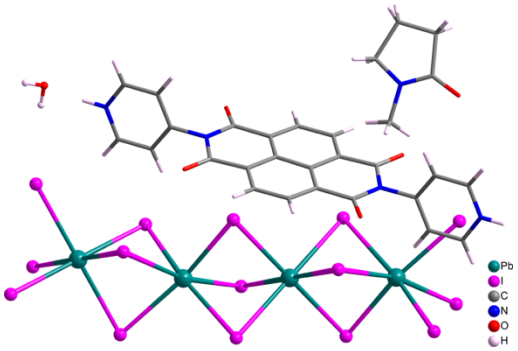

Figure S1. Portions of the X-ray structures of the hybrid crystal **1** composed of iodoplumbate nanowires and protonated naphthalene diimides.

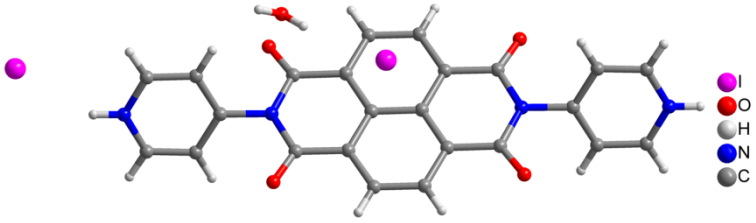

Figure S2. The X-ray structures of the $(H_2DPNDI)\cdot(2I)$.

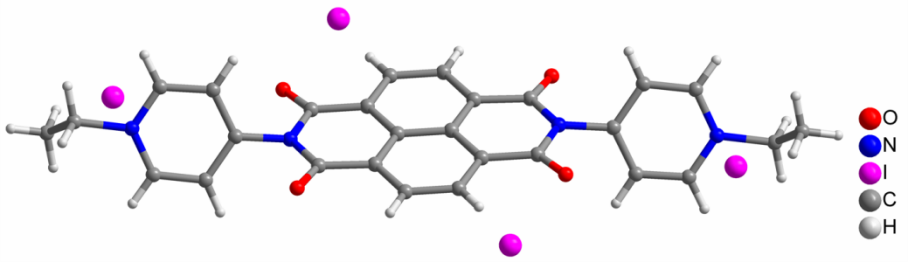

Figure S3. The X-ray structures of the $(Et_2DPNDI)\cdot(2I)$

3. UV/Vis diffuse reflectance spectra

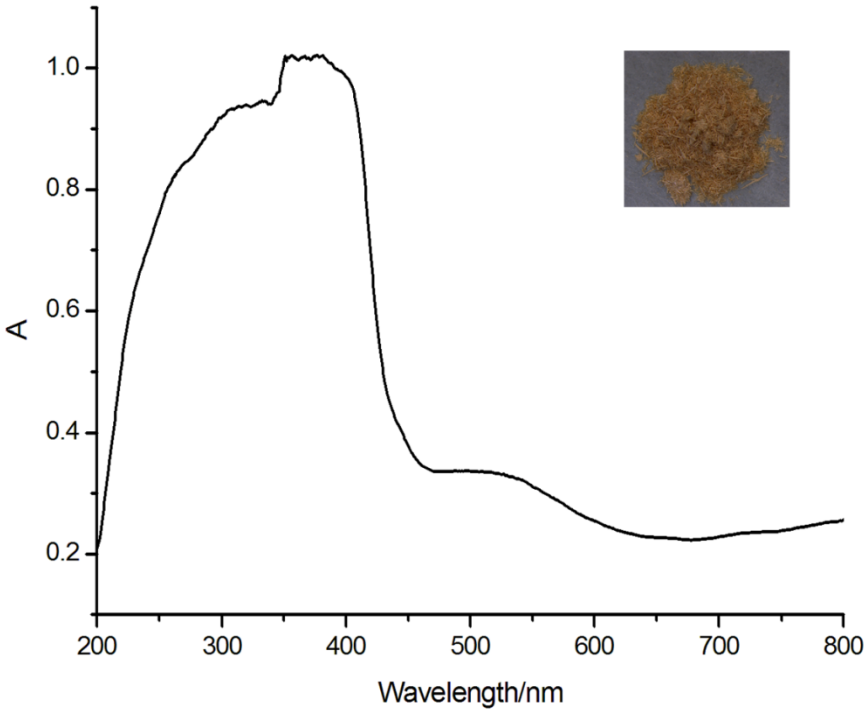

Figure S4. UV/Vis diffuse reflectance spectrum of DPNDI at room temperature.

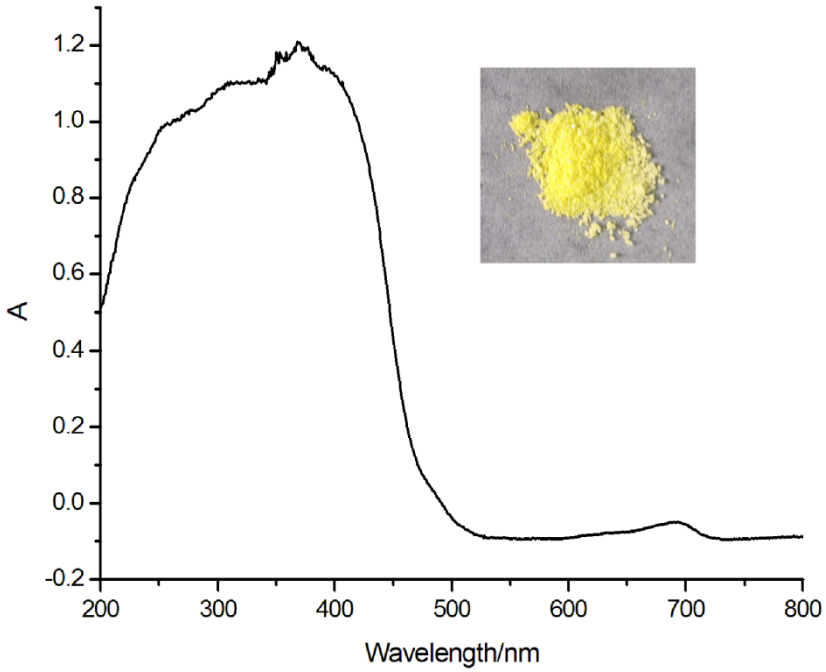

Figure S5. UV/Vis diffuse reflectance spectrum of $(Bu_4N)[PbI_3]$ at room temperature.[S3]

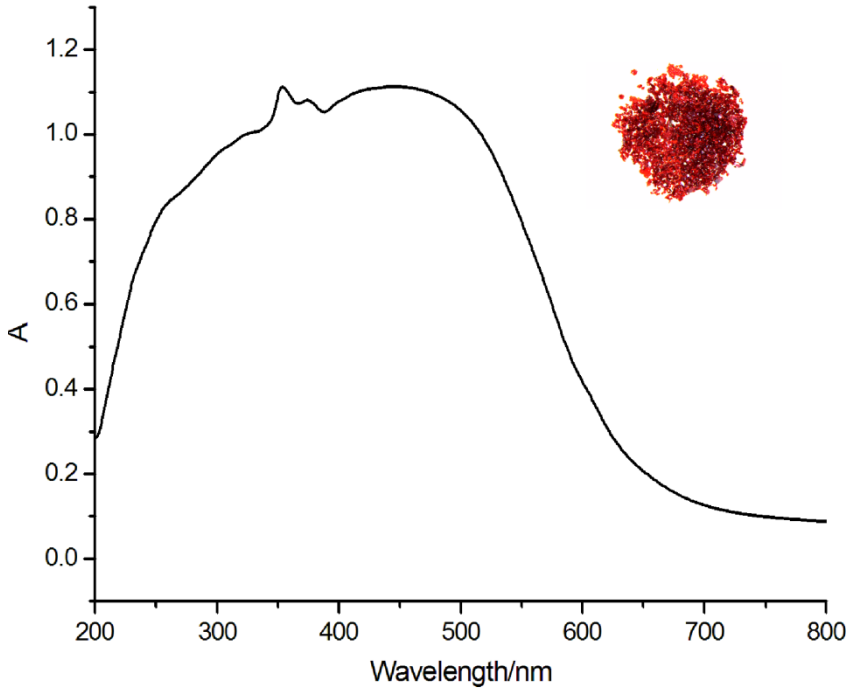

Figure S6. UV/Vis diffuse reflectance spectrum of $(H_2DPNDI)\cdot(2I)$ at room temperature.

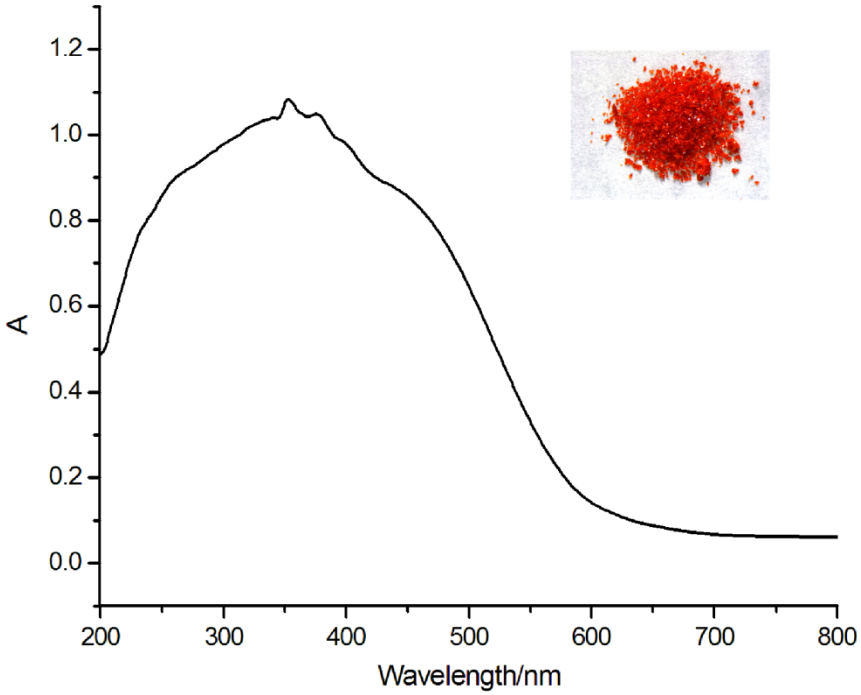

Figure S7. UV/Vis diffuse reflectance spectrum of $(Et_2DPNDI)\cdot(2I)$ at room temperature.

4. X-ray Powder Diffraction

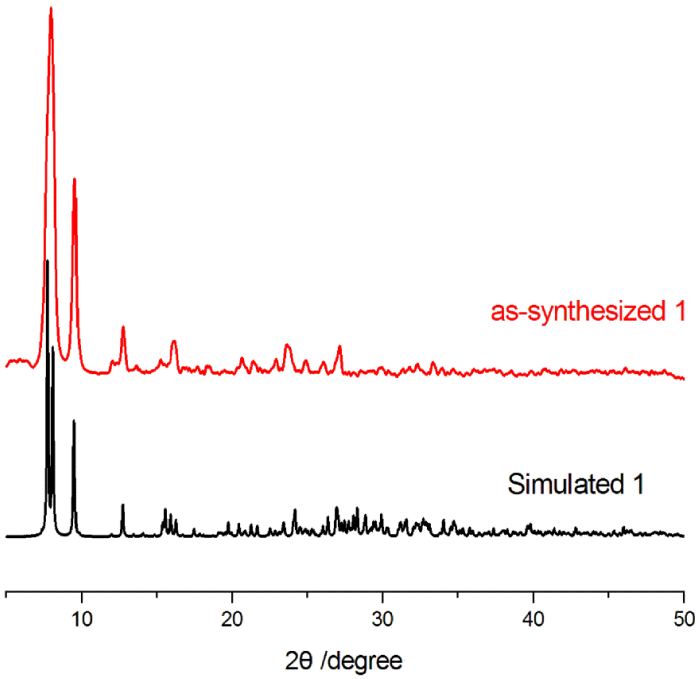

Figure S8. Comparison of the simulated and synthesized PXRD for complex **1**.

5. Thermogravimetric analyses

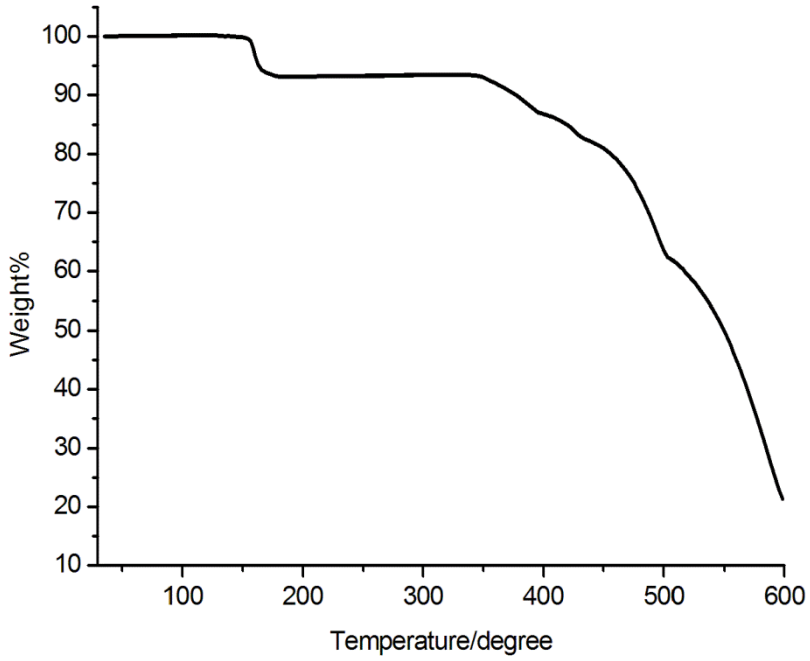

Figure S9. TGA data of **1**

6. References

S1. Guha, S.; Goodson, F. S.; Corson, L. J.; Saha. S. *J. Am. Chem. Soc.,* 2012, **134**, 13679.

S2. Sheldrick. G. *Acta Cryst.* 2008, **A**64, 112-122.

S3. Krautscheid, H. and Vielsack, F. *Angew. Chem. Int. Ed.,* 1995, **34**, 2035-2037.