Supporting information

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Synthesis of $[Cul(piperazine)_{0.5}]_{\infty}$

All reagents were purchased form Sigma-Aldrich and used without further purification. 0.5 mml of piperazine were dissolved in 15 mL of acetonitrile and 1 mmol of CuI was dissolved in 10 mL of hot acetonitrile (70°C). The piperazine was added to the CuI solution and suddenly a white precipitate appeared. The precipitate was filtered and washed with acetonitrile to eliminate traces of undissolved CuI. The crystal phase was checked by comparison of the observed X-ray powder pattern with the calculated one (figure 1).



Figure S1. Comparison of the observed diffractogram of the $[Cul(piperazine)_{0.5}]_{\infty}$ (green line) with the one calculated on the basis of the crystal structure XUJDAI (blue line).

Crystal of [Cul(piperazine) $_{0.5}$]_{∞}

Crystals suitable for X-ray single crystal diffraction and laser scanning confocal fluorescence microscopy were obtained by triple layer crystallization.

The lower layer was a saturated aqueous solution of KI with CuI, middle solution was ethanol and upper solution was a solution of acetonitrile with piperazine. Crystals appeared after one week.

X-Ray data

Crystal data were collected on an Oxford Xcalibur S instrument with MoKa radiation (λ =0.71073 Å) and graphite monochromator equipped with Oxford Cryosystem. SHELX97 was used for structure solution and refinement based on F². Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added in calculated positions. The crystal structure collected at 90K was affected by the presence of spurious peaks do to the formation of ice during the data collection (see Table S1).

X-ray powder diffractograms were collected on a Panalytical X'Pert PRO automated diffractometer with Cu_{Ka} radiation and a X'Celerator detector without monochromator. The program Mercury was used for the calculation of X-ray powder patterns on the basis of single-crystal data. In Table S2 are reported the Cu-Cu

distances observed in the crystal structures. The data have been deposited at the Cambridge Crystallographic Data Centre with numbers CCDC 1404771-1404773. The crystal structures can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/ci.

	XIUDAJ	Room	150K	90K
		temperature		
Formula	$C_4H_{10}Cu_2I_2$	$C_4H_{10}Cu_2I_2$	$C_4H_{10}Cu_2I_2$	$C_4H_{10}Cu_2I_2$
Lattice	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	C2/c	C2/c	C2/c	C2/c
a (Å)	9.309(2)	9.255(3)	9.2363(6)	9.209(2)
b (Å)	15.436(4)	15.294(3)	15.390(1)	15.433(3)
c (Å)	7.0974(16)	7.076(2)	7.0570(5)	7.043(1)
β (deg)	103.604(4)	103.45(3)	103.725(8)	103.72(2)
V (ų)	991.239	974.1(5)	974.49(11)	972.4(3)
Z,Z'	8, 0.5	8, 0.5	8, 0.5	8, 0.5
$ ho_{ m calcd} m Mg/m^3$	3.129	3.184	3.183	3.190
μ, mm ⁻¹	-	10.640	10.636	10.659
Measured/ independent	-	2181/1146	2112/1083	1782/1051
R _{int}	-	0.0267	0.0249	0.0939
R ₁	0.0298	0.0390	0.0281	0.0825
wR ₂	-	0.0751	0.0687	0.2319
argest diff. peak and hole(e. Å ⁻³)	-	0.926 and -0.797	0.948 and -1.030	4.952 and -2.778

Table S1 X-ray Crystallographic data

Table S2. Cu-Cu distances observed in the crystal structure

	d Cu—Cu (Å)	d Cu—Cu (Å)
XIUDAJ	2.771(1)	2.729(1)
RT	2.757(1)	2.714(2)
150 K	2.737(1)	2.702(1)
90 К	2.728(2)	2.696(2)

Data mining data

A search on the CSD V5.35 revealed the presence of only 18 Cul polymeric structures which can describe as double chain.^[1] Visual inspection has been done to assure the correct polymeric structure of the Cul. In Table S3 the REFCODEs and the Cu-Cu distances are reported. Depending on the symmetry present in the crystal structure form one up to three different distances have been found. Only three other structures (CEZBEQ, AGIYEU01 and HUJHUP, HUJHUP01: same structure but collected at different temperature) in addition to the XUJDAI present all Cu-Cu distances shorter than 2.8 Å.

Table S3. List of the REFCODE and the Cu-Cu distances

Refcode	d _{cu-cu} (Å)
CEZBEQ	2.730 - 2.771
AGIYEU01	2.756
CAJQOT	2.916 -2.886 - 3.439
CEPFOS	2.649 – 3.557
CISSOO	2.751- 3.279
ECEVIS	2.859 - 3.541 - 3.083
HALZAW	2.959 – 2.930
HUJHID	2.818
НИЈНИР	2.700 – 2.756
HUJHUP01	2. 722 – 2.775
LAGVAS	2.790 – 2.998
MUHQOV	2.778-3.414
MUHQOV01	2.797- 3.407
OMIHEX	2.846
ORUSAW	3.358 – 2.757
RIWXIF	2.643-2.718- 2.876
TAWKUZ	2.838 - 2.764- 2.721
VEVGUY	2.789 – 3.505
VIXBEK	2.827
XUJDAI	2.729 – 2.771

Luminescence spectroscopy and photophysics

Determinations at room temperature were performed on crystalline powder samples or crystal small needle crystals placed inside two quartz slides, whereas measurements at 77K made use of quartz capillary tubes immersed in liquid nitrogen in a cold finger quartz dewar. Emission and excitation spectra were collected in front-face mode using a Edinburgh FLS920 fluorimeter equipped with Peltier-cooled Hamamatsu R928 PMT (200-850 nm) or a Spex Fluorolog II fluorimeter, and corrected for the wavelength dependent phototube response. Luminescence lifetimes were measured with an IBH 5000F time-correlated single-photon counting apparatus, by using pulsed NanoLED excitation sources at 465 nm and 278 nm. Analysis of the luminescence decay profiles against time was accomplished with the Decay Analysis Software DAS6 provided by the manufacturer. Estimated errors are 10% on lifetimes and 3 nm on emission maxima.

Laser Scanning Confocal Fluorescence imaging

Measurements were performed on an inverted Nikon A1 laser scanning confocal microscope equipped with a CW Argon ion laser (Melles Griot) and a CW/pulsed diode laser emitting at 405 nm (PicoQuant GmbH, Berlin, Germany). Confocal fluorescence imaging was carried out on the samples at RT. The 521 x 512 pixel images were collected using a Nikon PLAN APO VC 20X objective with NA 0.75. With this imaging configuration, pixel side dimension ranged from 250 -400 nm. Hexagonal pinhole dimension was set to 1 au corresponding to 33 µm and optical thickness of 330 nm. In the scan head dichroic mirrors reflecting 405, 457nm, and 488 nm were used. Fluorescence intensity images were collected for several spectral windows using bandpass filters centered at 525 nm (50), and 595 (50). Spectral imaging has been performed using the Nikon A1 spectral detector consisting of a multi-anode photomultiplier with an array of 32 anodes. A wavelength range of 10 nm per anode has been applied.

Additional spectroscopic data



Figure S2. Corrected excitation a) and emission b) spectra of a powder sample of $[Cul(piperazine)_{0.5}]_{\infty}$ collected at the indicated emission or excitation wavelengths at room temperature.



Figure S3. Non-corrected normalized excitation-emission map of small needle crystals of $[Cul(piperazine)_{0.5}]_{\infty}$ at room temperature. The emission intensity for the excitation range 370-420 nm is multiplied by a factor 10.

Computational methods and additional results

Periodic calculations on the infinite crystalline structures have been carried out at the DFT level using the CRYSTAL^[2] quantum chemistry program, that uses a local basis set of Gaussian functions centred on atoms. A hybrid B3LYP functional has been adopted for all calculations.^[3] Hybrid functionals have been demonstrated to perform much better than standard LDA or GGA functionals in the description of band gaps.^[4]

The adopted basis set for all atoms except lodine is an all-electron triple-zeta valence basis (pob-TZVP) as specifically optimized for solids by Peintinger *et al.*.^[5] On lodine an effective core relativistic pseudopotential (ECP28MDF) taken from the Stuttgart pseudopotential database has been used to describe the 28 core electrons, in conjunction with the associated VTZ basis from the same database.^[6] As a first step, geometry has been fully optimized starting from the experimental XRD data. The geometrical

resulting parameters are reported in Tables S4 and S5.

Table S4 Lattice Parameters of Cul-Pip crystal optimied at the DFT (B3LYP) level.			
а	b	C	β
9.34729420	15.83515648	6.81851846	106.365893

Table S5 Fractional coordinates of irreducible atoms in the unit cell as optimized at the DFT	(B3LYP)	level

Atom	x/a	y/b	z/c
Ν	-0.3273	0.1684	-0.0130
Н	-0.3638	0.1597	-0.1674
С	-0.1624	0.1740	0.0424
Н	-0.1201	0.1173	-0.0124
Н	-0.1231	0.1733	0.2088
С	0.1083	-0.2526	0.0428
Н	0.1392	-0.2492	0.2093
Н	-0.0128	-0.2575	-0.0098
1	-0.3134	-0.0749	0.0033
Cu	-0.3804	0.0648	0.1196

The wavefunction computed at the equilibrium geometry was analyzed in order to gain further insight into the electronic structure of the system. In Figure S4 the crystalline orbitals close to the Fermi level have ben plotted using the DL Visualize (DLV) program developed by Barry Searle.^[7]



Figure S4 Pictorial representation of highest occupied and lowest unoccupied orbitals. Legenda: Big dark green spheres: I ; yellow: Cu ; light green: C; purple : N; grey: H

The computed band structure of the crystal is reported in Figure S5.



Figure S5. Computed band structure of the Cul-Piperazine crystal. Standard nomenclature of special k-points in the Brillouin Zone is adopted.

The UV-visible adsorption spectrum has been computed through a coupled-perturbed Kohn-Sham (CPKS) method taking into account the field frequency and implemented in the code CRYSTAL^[8] for calculating the high-frequency dielectric constant of semi-conductors till the first electronic transitions. The spectrum is obtained numerically from the complex dielectric function, and the results are completely analogous to those of a full TD-DFT treatment.

References

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