Supporting Information

A new subclass of copper (I) hybrid emitters showing TADF with near-unity quantum yields and a strong solvatochromic effect

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§1. General details and instrumentations

CuI (99%, Sigma-Aldrich), Ph₃P (99%, Sigma-Aldrich), MeCN (HPLC grade, Cryochrom), PhCN (99%, Sigma-Aldrich), were used as purchased. CH₂Cl₂ (ANT) and Me₂CO (Soyuzkhimprom) were distilled prior to use. Tris(2-pyridyl)phosphine was prepared following known procedure.¹

Powder X-ray diffraction analyses (PXRD) were made on a Shimadzu XRD-7000 diffractometer (Cu-K α radiation, Ni – filter, 3–35° 2 θ range, 0.03° 2 θ step, 5s per point).

The CHN microanalyses were performed on a MICRO cube analyzer.

Thermogravimetric analyses (TGA&DTG&c-DTA) were carried out in a closed Al₂O₃ pan under argon flow at 10 °C/min⁻¹ heating rate using a NETZSCH STA 449 F1 Jupiter STA instrument.

mid-IR spectra were recorded in *mid*-IR region on a Bruker Vertex 80 FT-spectrometer in KBr pellets at ambient temperature.

Diffuse reflectance spectra were registered on a Shimadzu UV-3101 spectrophotometer. Samples were prepared by a grinding of a complex (10 mol%) with BaSO₄. The reflectance data were further converted into absorption spectra applying a Kubelka–Munk function. Tauc plot was built using indirect band gap energy approximation, i.e. plotting $(\alpha hv)^2$ versus photon energy (hv).

Steady-state excitation and emission spectra were recorded on a Fluorolog 3 spectrometer (Horiba Jobin Yvon) equipped with a cooled PC177CE-010 photon detection module and an R2658 photomultiplier. The emission decays were recorded on the same instrument. The absolute PLQYs were determined at 298 K using a Fluorolog 3 Quanta-phi integrating sphere. Temperature-dependent excitation and emission spectra as well as emission decays were recorded using an Optistat DN optical cryostat (Oxford Instruments) integrated with above spectrometer. To investigate of solvate $2 \cdot 8 \text{CH}_2 \text{Cl}_2$, its freshly prepared crystals were placed in a cuvette and then covered with a small layer of dichloromethane.

§2. Synthesis and characterization data



Scheme 1. Synthesis and interconversion of complexes 1–3.

Compound 1.MeCN

To a stirring solution of CuI (32 mg, 0.168 mmol) in MeCN (3 mL), a solution of Py₃P (22 mg, 0.084 mmol) and Ph₃P (55 mg, 0.210 mmol) in acetonitrile (3 mL) was rapidly added. The reaction mixture was stirred at ambient temperature for 1 h. Thereafter, a yellowish precipitate formed was centrifuged and washed with MeCN (3 mL), and then dried in vacuum. Yellowish powder. Yield: 60 mg (59%). X-ray quality single crystals were obtained by vapor diffusion of diethyl ether into a MeCN solution of the complex. Anal. Calc. for $C_{53}H_{45}Cu_2I_2N_4P_3$ (1211.77): C, 52.5; H, 3.7; N, 4.6%. Found: C, 52.4; H, 3.8; N, 4.5%. FT-IR (KBr, cm⁻¹): 420 (w), 490 (m), 507 (vs), 528 (s), 694 (vs), 745 (vs), 772 (m), 997 (w), 1007 (m), 1026 (w), 1053 (w), 1092 (m), 1157 (w), 1184 (w), 1273 (w), 1279 (vw), 1433 (s), 1450 (m), 1477 (m), 1578 (m), 1630 (vw), 2247 (vw), 2855 (vw), 2914 (w), 3049 (w). ³¹P {¹H} NMR (202.47 MHz, DMSO-d⁶, ppm), δ : 3.28, -6.68, -28.15.

Compound 2

To a mixture of CuI (72 mg, 0.378 mmol), Ph₃P (50 mg, 0.191 mmol) and Py₃P (51 mg, 0.191 mmol), CH₂Cl₂ (3 mL) was added and the suspension was intensively stirred for 3 h. The resulting precipitate was centrifuged, washed with CH₂Cl₂ (3 mL), and dried in vacuum. Yellow powder. Yield: 120 mg (70%). X-ray quality single crystals of $2 \cdot 8$ CH₂Cl₂ were obtained by vapor diffusion of diethyl ether into a CH₂Cl₂ solution of the complex. According to thermogravimetry and microanalysis data, solvate $2 \cdot 8$ CH₂Cl₂ easily losses the solvate molecules to afford complex 2 itself. Anal. Calc. for C₆₆H₅₄Cu₄I₄N₆P₄ (1816.87): C, 43.6; H, 3.0; N, 4.6%. Found: C, 43.7; H, 3.1; N, 4.5%. FT-IR (KBr, cm⁻¹): 426 (w), 511 (vs), 528 (s), 694 (s), 745 (s), 775 (m), 1007 (m), 1047 (w), 1096 (m), 1157 (w), 1182 (w), 1233 (w), 1277 (w), 1425 (s), 1433 (s), 1450 (s), 1479 (m), 1560 (w), 1578 (s), 1624 (w), 2855 (vw), 2924 (w), 2970 (w), 3046 (w). ³¹P{¹H} NMR (202.47 MHz, DMSO-d⁶, ppm), δ : 3.29, -6.72, -30.27.

Compound 3-PhCN

A solution of Py₃P (60 mg, 0.226 mmol) and Ph₃P (120 mg, 0.458 mmol) in PhCN (3 mL) was added to a stirring suspension of CuI (130 mg, 0.683 mmol) in PhCN (3 mL). The reaction mixture was stirred for 5 h at ambient temperature. The resulting suspension was centrifuged and the obtained powder was washed with diethyl ether (2 × 3 mL) and dried in vacuum. Yellow powder. Yield 305 mg (92%). X-ray quality single crystals of **3**·PhCN were obtained by vapor diffusion of diethyl ether into a PhCN solution of the complex. Anal. Calc. for $C_{58}H_{47}Cu_3I_3N_4P_3$ (1464.29): C, 47.6; H, 3.2; N, 3.8%. Found: C, 47.4; H, 3.3; N, 3.7%. FT-IR (KBr, cm⁻¹): 411(w), 432 (w), 501 (s), 509 (s), 521 (vs), 548 (w), 694 (vs), 745 (vs), 760 (m), 773 (m), 849 (vw), 922 (vw), 997 (w), 1007 (m), 1028 (w), 1055 (w), 1096 (m), 1157 (w), 1283 (w), 1308 (vw), 1329 (vw), 1427 (s), 1435 (s), 1454 (m), 1479 (m), 1489 (w), 1578 (m), 1663 (vw), 1813 (vw), 1888 (vw), 1902 (vw), 1962 (vw), 2228 (w), 2953 (vw), 3005 (w), 3032 (w), 3048 (m). ³¹P{¹H} NMR (202.47 MHz, DMSO-d⁶, ppm), δ : 3.16, -6.61, -31.09.

Compound 3.1.5Me₂CO

To a dried powder of **3**·PhCN (100 mg, 0.068 mmol), acetone (5 mL) was added. The suspension was stirred for 5 h. Thereafter the suspension was centrifuged and the procedure was repeated two times. The resulting precipitate was dried in vacuum. Yield 86 mg (87%). Yellow powder. X-ray quality single crystals were obtained by vapor diffusion of diethyl ether into acetone solution of complex. Anal. Calc. for $C_{55.5}H_{51}Cu_3I_3N_3O_{1.5}P_3$ (1448.25): C, 46.0; H, 3.5; N, 2.9%. Found: C, 46.1; H, 3.3; N, 2.8%. FT-IR (KBr, cm⁻¹): 388 (w), 413 (w), 434 (w), 511 (s), 521 (vs), 694 (vs), 745 (s), 773 (m), 1007 (w), 1096 (m), 1157 (w), 1221 (w), 1281 (w), 1362 (w), 1435 (s), 1452 (m), 1479 (m), 1578 (m), 1709 (m), 2851 (w), 2922 (w), 3003 (w), 3051 (m). ³¹P{¹H} NMR (202.47 MHz, DMSO-d⁶, ppm), δ : 3.21, -6.67, -31.19.

§3. Single crystal X-ray crystallography

The data for $2 \cdot 8 \text{CH}_2 \text{Cl}_2$ and $3 \cdot 1.5 \text{Me}_2 \text{CO}$ were collected on an automated Agilent Xcalibur diffractometer equipped with an area AtlasS2 detector (graphite monochromator, $\lambda(\text{MoK}\alpha) = 0.71073$ Å, ω -scans with a step of 0.25° and 0.5°). Integration, absorption correction, and determination of unit cell parameters were performed using the CrysAlisPro program package.² The data for 1 ·MeCN and 3 ·PhCN were collected on a Bruker Kappa Apex II CCD diffractometer using ϕ, ω -scans of narrow (0.5°) frames with MoK α radiation ($\lambda =$ 0.71073 Å) and a graphite monochromator. Absorption corrections were applied using the empirical multiscan method with the SADABS program.³ The structures were solved by dual space algorithm (SHELXT⁴) and refined by the full-matrix least squares technique (SHELXL⁵) in the anisotropic approximation (except hydrogen atoms). The positions of the hydrogen atoms were calculated with the riding model. The structure of 3 ·1.5Me₂CO contains void volume occupied with highly disordered acetone guest molecules, which could not be refined as a set of discrete atomic positions. The final composition of the compound 3 ·1.5Me₂CO was defined according to PLATON/SQUEEZE⁶ procedure (191 e^- in 777 Å³ correspond to 6 acetone molecules per unit cell) and the data of element (C, H, N) analyses. The crystallographic data and details of the refinements are summarized in Table S1.

	1·MeCN	$2 \cdot 8 CH_2 Cl_2$	3·PhCN	3 ·1.5Me ₂ CO
CCDC number	2046363	2045855	2046361	2045854
Chemical formula	$C_{53}H_{45}Cu_2I_2N_4P_3$	$C_{74}H_{70}Cl_{16}Cu_4I_4N_6P_4$	$C_{58}H_{47}Cu_{3}I_{3}N_{4}P_{3} \\$	$C_{55.50}H_{51}Cu_3I_3N_3O_{1.50}P_3$
$M_{ m r}$	1211.72	2496.20	1464.22	1448.22
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, P ⁻¹	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$
Temperature (K)	296	130	200	130
a, b, c (Å) α, β, γ (°)	19.3560(15), 14.3616(12), 20.5605(18) 118.060 (3)	12.32556(19), 12.5965(2), 14.6574(3) 97.7266(15), 95.1796(15), 93.0511(13)	17.1143(10), 17.8898(11), 18.7126(8)	16.0496(8), 18.3670(7), 18.5626(9)
$V(Å^3)$	5043.6 (7)	2240.90 (7)	5729.3 (5)	5471.9 (4)
Ζ	4	1	4	4
μ (mm ⁻¹)	2.20	2.91	2.84	2.98
Crystal size (mm)	$0.50 \times 0.20 \times 0.10$	$0.22\times0.14\times0.02$	$0.15 \times 0.10 \times 0.10$	$0.22\times0.21\times0.14$
T_{\min} , T_{\max}	0.524, 0.745	0.904, 1.000	0.852, 0.928	0.724, 1.000
No. of measured, independent and observed [<i>I</i> > 2s(<i>I</i>)] reflections	73506, 8894, 6585	18310, 9781, 8032	90098, 15774, 11318	19606, 10419, 9655
$R_{\rm int}$	0.045	0.025	0.066	0.038
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.596	0.680	0.705	0.617
$R[F^2 > 2s(F^2)],$ $wR(F^2), S$	0.039, 0.105, 1.07	0.030, 0.060, 0.99	0.041, 0.099, 1.01	0.042, 0.102, 1.04
No. of reflections	8894	9781	15774	10419
No. of parameters	578	487	640	587
$\Delta \rho_{max}$, $\Delta \rho_{min}$ (e Å ⁻³)	0.87, -0.67	0.88, -0.47	2.27, -1.64	1.00, -0.73

Table S1. Data collection and selected refinement parameters for the obtained complexes.



Figure S1. X-Ray derived structure of **1**·MeCN. Solvent molecules and hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (°): I1–Cu1 2.6915(7), I2–Cu1 2.6633(7), Cu2–N3 2.050(4), Cu2–N2 2.056(4), Cu2–N1 2.059(4), Cu2–P3 2.1713(14), Cu1–P1 2.2777(14), Cu1–P2 2.2951(14), N3–Cu2–N2 95.92(17), N3–Cu2–N1 94.14(17), N2–Cu2–N1 93.58(18), N3–Cu2–P3 123.26(13), N2–Cu2–P3 120.81(12), N1–Cu2–P3 121.83(12), P1–Cu1–P2 118.59(5), P1–Cu1–I2 107.31(4), P2–Cu1–I2 112.71(4), P1–Cu1–I1 102.71(4), P2–Cu1–I1 104.95(4).



Figure S2. X-Ray derived structure of $2 \cdot 8 \text{CH}_2 \text{Cl}_2$. Solvate molecules and hydrogen atoms are omitted for clarity. Note that this complex lies about an inversion centre; the atoms with the "A" labels are at equivalent positron (-x, -y, 1-z). Selected bond length (Å) and angles (°): Cu1–I1 2.6344(4), Cu1–I2 2.6596(4), Cu1–I2A 2.6848(4), Cu1–P1 2.2372(8), Cu2–N1 2.053(3), Cu2–N2 2.046(2), Cu2–N3 2.063(2), Cu2–P2 2.1711(8), I1–Cu1–I2 108.330(14), I1–Cu1–I2 110.362(14), I2–Cu1–I2 8.447(13), P1–Cu1–I1 109.55(2), P1–Cu1–I2 109.79(2), P1–Cu1–I2 110.35(3), N1–Cu2–N3 97.44(10), N1–Cu2–P2 121.05(7), N2–Cu2–N1 93.12(9), N2–Cu2–N3 92.90(9), N2–Cu2–P2 131.14(7), N3–Cu2–P2 113.59(7), Cu1–I2–Cu1 71.552(13).



Figure S3. X-Ray derived structure of **3**·PhCN. Solvate molecules and hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (°): I1–Cu1 2.6640(10), I1–Cu2 2.7417(11), I2–Cu1 2.6448(11), I2–Cu2 2.6859(11), I3–Cu1 2.6764(11), I3–Cu2 2.7647(12), Cu1–P2 2.1851(17), Cu1–Cu2 2.4912(12), Cu2–P1 2.2040(19), Cu3–N2 2.036(6), Cu3–N3 2.058(5), Cu3–N1 2.060(6), Cu3–P3 2.1641(19), Cu1–I2–Cu2 55.72(3), Cu1–I3–Cu2 54.47(3), P2–Cu1–Cu2 177.32(7), P2–Cu1–I2 116.92(6), Cu2–Cu1–I2 62.98(3), P2–Cu1–I1 118.22(6), Cu2–Cu1–I1 64.16(3), Cu1–I1–Cu2 54.86(3), I2–Cu1–I1 100.76(3), P2–Cu1–I3 102.67(4), I1–Cu1–I3 102.90(4), P1–Cu2–Cu1 176.27(7), P1–Cu2–I2 120.71(6), Cu1–Cu2–I2 61.30(3), N2–Cu3–P3 126.60(16), N3–Cu3–P3 116.07(16), N1–Cu3–P3 121.31(16).



Figure S4. X-Ray derived structure of **3**·1.5Me₂CO. Solvate molecules and hydrogen atoms are omitted for clarity. Note that the solvent molecules were not located and that their contributions to the structure factors were removed by the use of SQUEEZE. Selected bond length (Å) and angles (°): Cu1–Cu2 2.4873(14), Cu1–I1 2.6534(12), Cu1–I2 2.624(3), Cu1–I3 2.701(2), Cu1–P1 2.186(2), Cu2–I1 2.7196(13), Cu2–I2 2.736(3), Cu2–I3 2.755(2), Cu2–P2 2.203(2), Cu3–N1 2.061(6), Cu3–N2 2.068(7), Cu3–N3 2.050(7), Cu3–P3 2.170(2), Cu2–Cu1–I1 63.78(4), Cu2–Cu1–I2 64.66(8), Cu2–Cu1–I3 63.99(5), I1–Cu1–I3 96.09(8), I2–Cu1–I1 101.33(9), I2–Cu1–I3 109.40(8), P1–Cu1–Cu2 175.86(8), P1–Cu1–I1 120.14(7), P1–Cu1–I2 114.55(10), P1–Cu1–I3 113.30(8), Cu1–Cu2–I1 61.08(4), Cu1–Cu2–I2 60.09(7), Cu1–Cu2–I3 61.77(5), I1–Cu2–I2 96.87(8), I1–Cu2–I3 93.33(8), I2–Cu2–I3 104.64(8), P2–Cu2–Cu1 171.71(8), P2–Cu2–I1 127.21(7), P2–Cu2–I2 115.82(9), P2–Cu2–I3 114.78(8), N1–Cu3–N2 94.3(3), N3–Cu3–N1 96.6(3),

N3-Cu3-N2 93.7(3), N3-Cu3-P3 128.43(19), Cu1-I1-Cu2 55.14(3), Cu1-I2-Cu2 55.25(6), Cu1-I3-Cu2 54.24(5).

§4. Powder X-ray diffraction data



Figure S5. Experimental and simulated PXRD patterns of the synthesized compounds.

§5. TG&DTA curves





Figure S6. TGA and DTG curves for the synthesized compounds.

§6. FT-IR spectra



Figure S7. mid-IR spectra of the synthesized compounds.



Figure S8. (*a*) Powder samples of the synthesized complexes under daylight; (*b*) Absorption spectra (plotted as Kubelka-Munk function) of these samples; (*c*) Tauc plots derived from the absorption spectra.



Figure S9. (*a*) Excitation spectra of 1·MeCN at different temperatures ($\lambda_{em} = 525 \text{ nm}$); (*b*) Emission spectra of 1·MeCN at different temperatures ($\lambda_{ex} = 350 \text{ nm}$).



Figure S10. (*a*) Excitation spectra of **2** at different temperatures ($\lambda_{em} = 540 \text{ nm}$); (*b*) Emission spectra of **2** at different temperatures ($\lambda_{ex} = 350 \text{ nm}$).



Figure S11. (*a*) Excitation spectra of 3·PhCN at different temperatures ($\lambda_{em} = 515 \text{ nm}$); (*b*) Emission spectra of 3·PhCN at different temperatures ($\lambda_{ex} = 300 \text{ nm}$).



Figure S12. (*a*) Excitation spectra of 3.1.5Me₂CO at different temperatures ($\lambda_{em} = 510$ nm); (*b*) Emission spectra of 3.1.5Me₂CO at different temperatures ($\lambda_{ex} = 350$ nm).

§8. Determination of singlet-triplet splitting energies

To evaluate singlet-triplet splitting energies $\Delta E(S_1-T_1)$ for hybrid complexes **1–3**, the experimental $\tau(T)$ datasets (Fig. 2c in main document) were fitted using Boltzmann type equation (Eq. S1) proposed for TADF model:⁷

$$\tau(T) = (3 + \exp\left(-\frac{\Delta E(S1 - T1),}{k_B T}\right)) / (\frac{3}{\tau_T} + \frac{1}{\tau_S} exp^{[to]}(-\frac{\Delta E(S1 - T1),}{k_B T}))$$
(Eq. S1)

where τ_S and τ_T are the decay times of the S₁ and T₁ excited states, respectively, and k_B is the Boltzmann constant. The resulting $\Delta E(S_1-T_1)$ values are outlined in Table 1 of the main document.

§9. Solvatochromic luminescence of 1·MeCN

As stated in the main text, solvate $1 \cdot \text{MeCN}$ loses its lattice MeCN molecules upon grinding with a pestle for about 1 min (Fig. S13a). TGA, IR and microanalysis data of the formed amorphous powder 1 (see PXRD pattern in Fig. 3b) agree with its formulation. So, the IR spectrum of 1 closely resembles that of $1 \cdot \text{MeCN}$, but does not contain v_{CN} vibration band from the MeCN lattice molecules (Fig. S13b). Again, the TGA curves of 1 and $1 \cdot \text{MeCN}$ differ only in the first step (144–155 °C) associated with the loss of lattice MeCN molecules of $1 \cdot \text{MeCN}$ (Fig. S13c). Ground powder 1, when treated with MeCN, quickly and quantitively transforms into $1 \cdot \text{MeCN}$. The completeness of this transformation is confirmed by PXRD and microanalysis data for the recovered $1 \cdot \text{MeCN}$. Besides, the recovered sample of $1 \cdot \text{MeCN}$ shows about the same emission properties as those of the parent solvate $1 \cdot \text{MeCN}$.



Figure S13. (*a*) Photoluminescence of solvate $1 \cdot \text{MeCN}$ and parent complex 1. Grinding the solvate $1 \cdot \text{MeCN}$ in a mortar for 1 min leads to the loss of the solvate molecule. The initial solvate $1 \cdot \text{MeCN}$ can be quantitatively recovered by treatment of 1 with several drops of MeCN at 298 K; (*b*) mid-IR spectra of 1 and $1 \cdot \text{MeCN}$; (*c*) TGA curves of 1 and $1 \cdot \text{MeCN}$.

§10. PDOS calculations of 1–3

The density of states was calculated using the Cambridge Serial Total Energy Package (CASTEP).⁸ Crystal structures obtained from single-crystal X-ray analysis were used directly without modification. Generalized gradient approximations (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional (xc) were used for all calculations. In all calculations, ultrasoft pseudopotentials were used for all chemical elements and the plane wave basis cut-off was set as 351 eV, the total energy tolerance was set to be 1×10^{-5} eV/atom.

The calculated bandgaps of all three compounds are well in trend with their experimental optical bandgap values, but have relatively smaller values. This is because the calculation used generalized gradient approximation (GGA) functional, which is well known to underestimate the bandgaps.⁹



Figure S14. Calculated total density of states (DOS) and projected density of states (PDOS) (component contributions) of title compounds.



Figure S15. Calculated total density of states (DOS) and projected density of states (PDOS) (atomic orbitals contributions) of title compounds.



Figure S16. Calculated contributions from lattice molecules (MeCN, CH₂Cl₂, and PhCN) in title compounds.

§11. DFT calculations of discrete molecule 1

Computation details

Quantum chemical calculations for the discrete molecule of **1** were performed in ADF2017 program suite.^{10–12} The dispersion corrected S12g density functional,¹³ all-electron TZP basis set¹⁴ and ZORA scalar relativistic approach¹⁵ was used for geometry optimization of complex **1** in the S₀, S₁ and T₁ states. The fully optimized geometries are characterized by the absence of the imaginary frequencies that confirms the local minima of the obtained forms of the complex. In order to obtain the electronic structure of the complex, the single point calculations at the optimized geometries was performed with dispersion corrected hybrid S12h density functional,¹³ all-electron TZP basis set and ZORA scalar relativistic approach.¹⁶



Figure S17. Selected molecular orbitals of ground (S_0) state of **1**. Cu (orange), I (green), P (violet), N (blue), C (gray). The hydrogen atoms are omitted for clarity.



Figure S18. Absorption spectrum of solid 1 (plotted as K-M function, 298 K) and calculated absorption patterns (vertical bars) for 1.



Figure S19. Optimized geometries and relative energies of 1 in the ground and lowest excited states. The Cartesian coordinates of these structures are collected in a separate supporting txt-file.



Figure S20. Overlay of the optimized S_0 and T_1 state geometries of 1.



Figure S21. Spin density distribution in the T_1 state of **1**.

§12. X-Ray radioluminescence

X-ray radioluminescence (RL) spectra were recorded on a home-built spectrometer¹⁷ following the earlier developed protocol for powder samples;¹⁸ further technical details on possible experimental artifacts and spectral processing can be found in ref.¹⁹ The sample of neat solid in the form of an island of finely ground powder with dimensions 3 x 8 mm and thickness of about 0.1 mm, applied via a stencil on a vertical aluminum plate with polypropylene-based double-sided Scotch tape, was directly exposed to the incident X-ray beam (unfiltered bremsstrahlung from a CW X-ray tube 2,5BSV-27-Mo, Svetlana, St. Petersburg, Russia, 40 kV x 20 mA, sample distance to anode 210 mm) and to the light-collecting optics of the detection system comprising a quartz optical imaging system, a grating monochromator (MDR-206, LOMO Photonics, St Petersburg, Russia, objective focus length 180 mm, grating 1200 lines per mm, inverse linear dispersion 4.3 nm mm⁻¹) with slits set to 2.2 mm/2.2 mm (spectral resolution about 10 nm), and a Hamamatsu H10493-012 photosensor module. All experiments were performed at ambient conditions in air without environmental control. To assess compound stability under X-ray irradiation, four consecutive spectra of single wavelength scans of 18 min each were recorded from freshly prepared samples, the gradual sagging of spectra is indicative of the degradation rate of unprotected neat powder under irradiation in air. The RL spectra given in the main text are averages of the four spectra. All RL spectra were recorded in nominally identical conditions and were normalized to sample amount in moles, the y-axes, although given in "arbitrary units", can be directly compared between different spectra. For quantification of luminous efficiency of the samples studied, RL of a reference sample of bismuth germanate (BGO) was also recorded using the same procedure. In the RL spectra, the emission line was integrated up to line maximum to produce AUC values, and the ratio of AUC value for the sample to AUC value for BGO was taken as the measure of luminous efficiency χ_E (Table S2).



Figure S22. Comparison of photoluminescence (PL) and radioluminescence (RL) spectra of 1-3 (298 K).





Figure S23. Comparison of X-ray stability of 1–3.

Table S2. Radioluminescence efficiency of 1–3 relative to BGO (reference).

СР	λ_{max}, nm	AUC, a.u.	$X_E = AUC/AUC_{BGO}$
1·MeCN	517	$2.0 imes 10^6$	1.0
2	557	$7.3 imes 10^5$	0.37
3·PhCN	533	2.4×10^{6}	1.2
BGO	485	$2.0 imes 10^6$	1.0





Figure S24. Check of linearity of RL response *vs.* dose rate for **1**–**3**. Detection wavelength was set at emission maximum, and emission intensity as raw signal from detector was recorded while varying anode current of the X-ray tube from nominal (20 mA) down to 5mA and back to 20 mA in 1 mA steps, recording signal for 1 min at each step (2 min at 5 mA). The accelerating voltage was held constant (40 kV), and thus anode current was directly proportional to dose rate, so the produced graph gives the dependence of emission intensity on dose rate over 4:1 range, clearly demonstrating a linear dose rate response. Upon returning back to nominal anode current the signal does not return exactly to the initial level due to sample degradation, as shown in Fig. S23 above.

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