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Effective solvent-free synthetic method for obtaining benzoate-pentafluorobenzoate europium(III) compound

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I. Synthetic data

Synthesis of all obtained compounds was carried out in air using $Eu(OAc)_3 \cdot 4H_2O$ (99.99%, «Lankhit »), benzoic acid (H(bz), 99%, « SLR»), pentafluorobenzoic acid ($H(F_5b)$, 99%, "P&M-Invest").

Infrared spectra of the complexes were recorded in the frequency range 4000–400 cm^{-1} on a Perkin-Elmer Spectrum 65 Fourier transform infrared spectrometer equipped with Quest ATR Accessory (Specac).

Elemental CHNS analysis of the synthesized compounds was carried out on a EuroEA 3000 CHNS analyzer (EuroVector, S.p.A.).

The powder diffraction patterns were obtained using the Bruker D8 Advance diffractometer with a LynxEye detector in Bragg-Brentano geometry. The sample was finely dispersed on a silicon holder with a zero background, $\lambda(CuK\alpha) = 1.54060$ Å. The acquired data were refined using the Topas 4 software [S1].

Photoluminescence excitation, emission spectra, and luminescence decays were recorded at room temperature with a Horiba-Jobin-Yvon Fluorolog-QM spectrofluorimeter equipped with a 75 W ArcTune xenon lamp and a Hamamatsu R-FL-QM-R13456 photomultiplier sensitive in the 200-980 nm emission range. The luminescence quantum yield (Φ) values were measured by absolute method, employing the same setup equipped with a G8 Spectralon®- covered sphere (GMP SA, Switzerland) and Hamamatsu R13456 photomultiplier. A diffusing screen was mounted inside the sphere to avoid direct irradiation of the detector. The measurements were carried out at ambient temperature. The samples in quartz cells were placed near the center of the sphere. A NIST-traceable 45 W quartz tungsten-halogen bulb emission standard (Oriel) was employed to measure the instrument response function. All QY measurements were repeated at least three times to achieve an experimental error below 15%.

Synthesis of $\{Eu(F_5b)_3\}$ (1)

$Eu(OAc)_3 \cdot 4H_2O$ (0.500 g, 1.247 mmol) was placed in a glass crystallizing dish, and pentafluorobenzoic acid (2.379 g, 11.222 mmol) was added. The mixture was stirred with a glass rod until a homogeneous mixture was formed. The resulting reaction mixture was heated to the melting point of pentafluorobenzoic acid (T_m = 107 °C) [S2], and dissolution of europium acetate in the molten acid was observed. The resulting melt was heated for 10 h with periodic stirring using a glass rod until the formation of a homogeneous solid product due to the sublimation of excess pentafluorobenzoic acid. The obtained product was washed with hexane and dried in air. The composition of the product was confirmed by CHN elemental analysis and IR spectroscopy. The product yield was 0.895 g (91%) based on $Eu(OAc)_3 \cdot 4H_2O$.

Found, %: C 32.1;

For $C_{21}O_6EuF_{15}$

Calculated, %: C 32.3;

IR (ATR), ν/см$^{-1}$: 3066 w, 2981 w, 2856 w, 2553 w, 2171 w, 1974 w, 1920 w, 1793 w, 1677 m, 1597 m, 1535 s, 1500 m, 1397 s, 1292 m, 1176 m, 1068 m, 1025 m, 933 m, 856 m, 709 s, 682 m, 620 w.

Synthesis of $\{Eu(bz)_3\}$ (2)

Compound **2** was obtained according to the procedure described for compound **1** using benzoic acid (1.369 g, 11.222 mmol) instead of pentafluorobenzoic acid. The reaction mixture was heated to the melting point of benzoic acid (T_m = 122 °C) [S3]. The obtained product was washed with hexane and dried in air. The composition of the product was confirmed by CHN elemental analysis and IR spectroscopy. The product yield was 0.575 g (89%) based on $Eu(OAc)_3 \cdot 4H_2O$.

Found, %: C 48.4, H 3.0;

For $C_{21}O_6EuH_{15}$

Calculated, %: C 48.6, H 2.9;

IR (ATR), ν/см$^{-1}$: 2998 w, 2360 m, 2337 w, 1868 m, 1828 w, 1793 w, 1772 w, 1733 w, 1702 m, 1650 s, 1589 s, 1525 s, 1492 m, 1398 s, 1361 m, 1278 w, 1116 m, 997 s, 935 m, 827 m, 769 m, 742 m, 690 w, 619 w, 582 w

Synthesis of [Eu(H(bz))(bz)(F$_5$b)$_2$]$_n$ (3)

Method 1

Europium pentafluorobenzoate (**1**) (0.200 g, 0.255 mmol) was placed in a glass crystallizing dish, and benzoic acid (0.155 g, 1.275 mmol) was added. The mixture was stirred with a glass rod until a homogeneous mixture was formed. The resulting reaction mixture was heated to the melting point of benzoic acid (Tm = 122 °C) [S3], and dissolution of europium pentafluorobenzoate in the molten acid was observed. The resulting melt was heated for 6 h with periodic stirring using a glass rod until the formation of a homogeneous solid product due to the sublimation of benzoic acid. The obtained product was washed with hexane and dried in air. The composition of the product was confirmed by CHN elemental analysis and IR spectroscopy. The product yield was 0.172 g (83%) based on europium pentafluorobenzoate.

Method 2

Europium benzoate (**2**) (0.132 g, 0.255 mmol) was placed in a glass crystallizing dish, and pentafluorobenzoic acid (0.270 g, 1.275 mmol) was added. The mixture was stirred with a glass rod until a homogeneous mixture was formed. The resulting reaction mixture was heated to the melting point of pentafluorobenzoic acid (Tm = 107 °C) [S2], and dissolution of the starting salt in the molten acid was observed. The resulting melt was heated for 4 h with periodic stirring using a glass rod until the formation of a homogeneous solid product due to the sublimation of benzoic acid. The obtained product was washed with hexane and dried in air. The composition of the product was confirmed by CHN elemental analysis and IR spectroscopy. The product yield was 0.163 g (79%) based on europium benzoate.

Single crystals suitable for SCXRD were obtained by slow evaporation of a solution of compound **3** (0.030 g) in dichloromethane (35 mL) at room temperature.

Found, %: C 41.4, H 1.3;

For $C_{28}O_8EuF_{10}H_{10}$

Calculated, %: C 41.2, H 1.2;

IR (ATR), ν/см$^{-1}$: 2414 w, 1828 w, 1735 w, 1698 m, 1644 m, 1610 s, 1577 m, 1521 m, 1494 s, 1455 m, 1407 s, 1353 m, 1108 m, 1072 w, 995 m, 935 w, 829 w, 775 m, 740 m, 715 s, 688 w, 674 w, 622 w, 561 w

II. Supplementary PXRD data

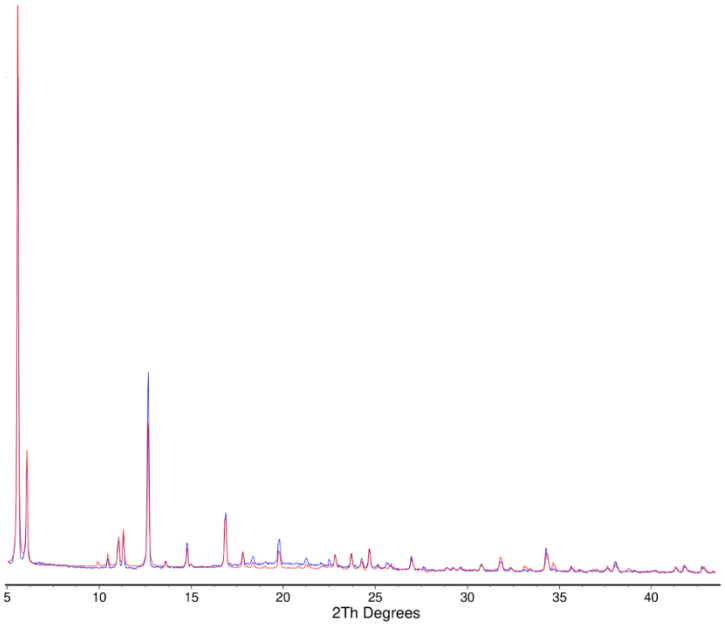
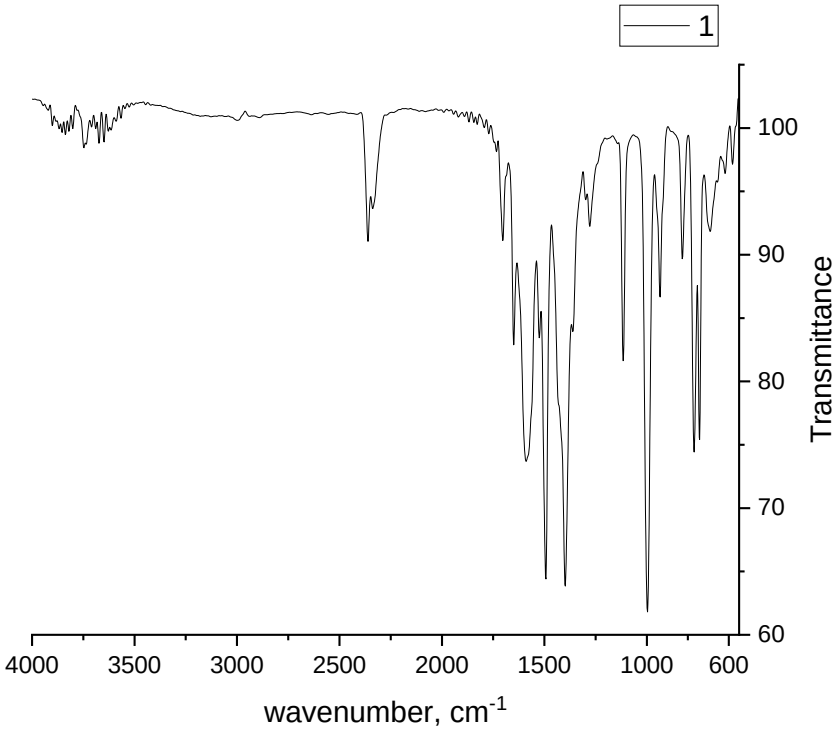
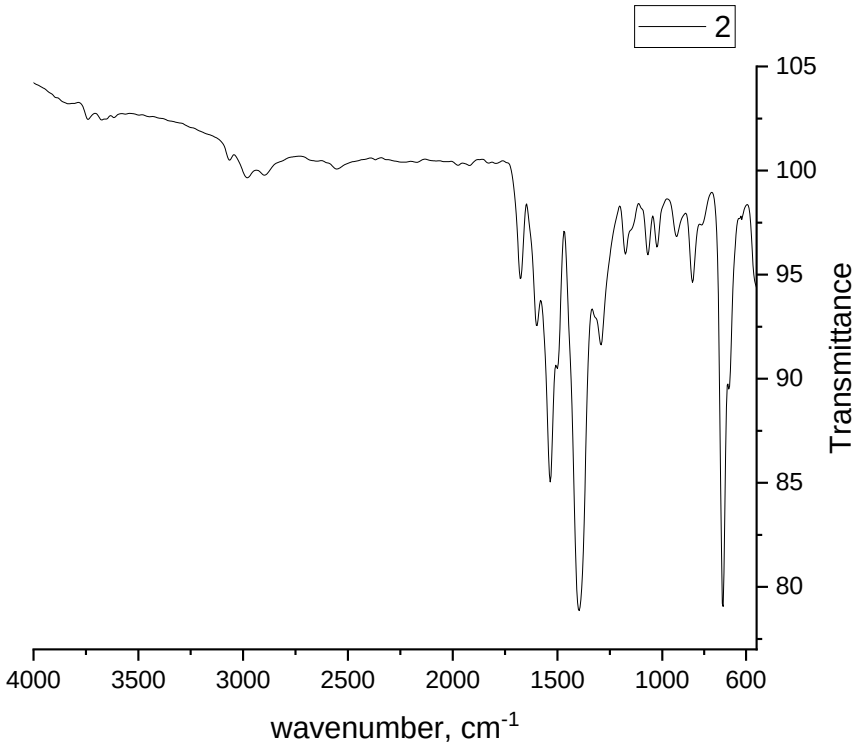


Figure S1. Comparison of experimental (blue) and calculated (red) powder X-ray diffraction patterns for compound **3**.

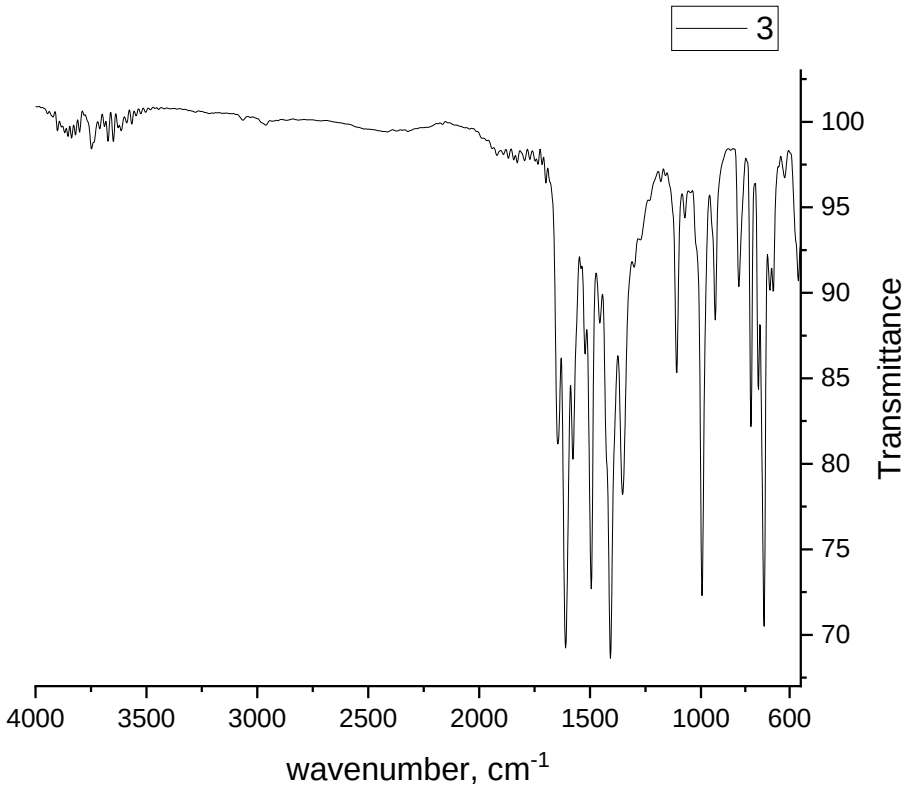
III. IR spectra of compounds



a)



b)



c)

Figure S2. IR spectra of compounds **1**(a), **2**(b), **3**(c).

IV. Supplementary structural data

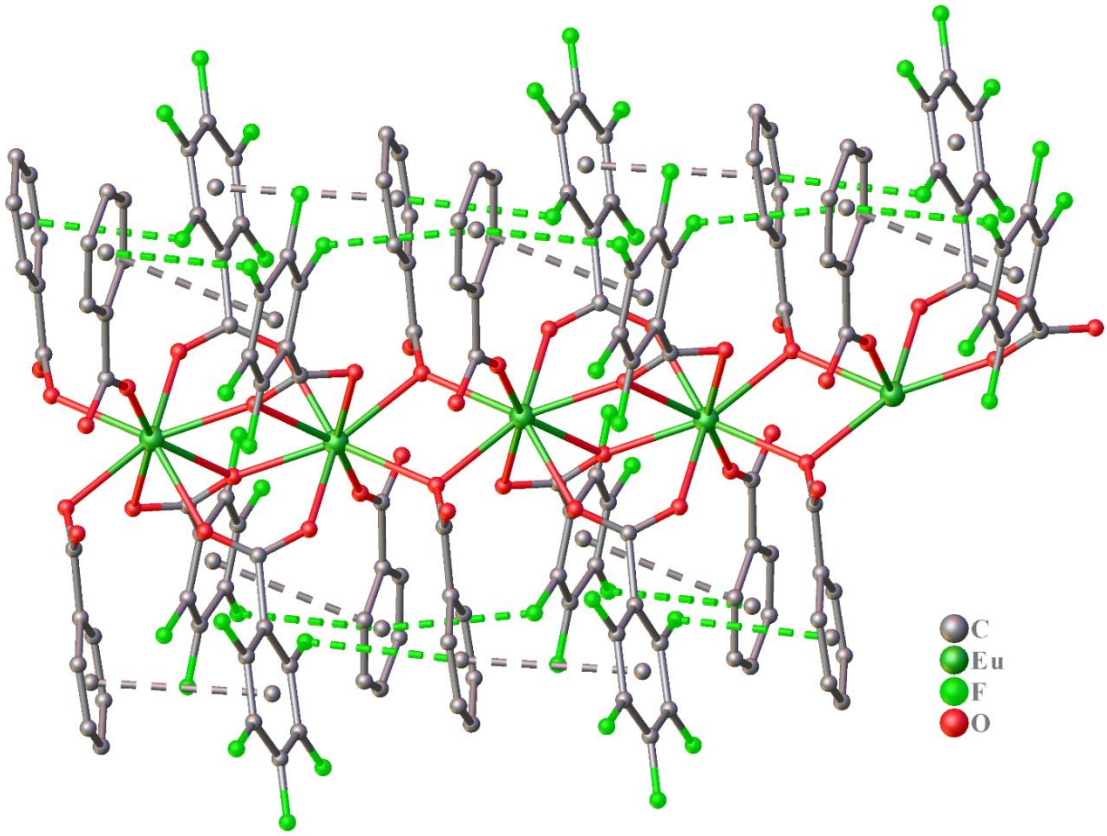


Figure S3. Fragment of the polymer chain of compound **3**. π···π and C-F···π interactions are shown as dashed lines. Hydrogen atoms are omitted for clarity.

Table S1. Table of π···π interactions in crystal packing of complex **3**.

Interactions	Cg···Cg, Å	Cg···Perp, Å	Symmetry code	α, deg
F_5b···bz	3.784(4)	3.417(3)	1-x,1-y,1-z	12.7(3)
F_5b ···H(bz)	3.812(4)	3.455(3)		6.3(3)

Table S2. C-F···π interactions in the crystal packing of complex **3**.

Interaction	F···Cg, Å	Symmetry code	F···Perp, Å	C-F···Cg,^{O}
C(3)–F(3)··· π(bz)	3.615(5)	1-x,1-y,1-z	3.156	71.5(3)
C(7)–F(7)··· π(bz)	3.480(5)	-x,1-y,1-z	3.327	82.9(3)
C(10)–F(10)··· π(bz)	3.432(5)	1+x,y,z	3.324	97.2(3)
C(12)–F(12)··· π(H(bz))	3.606(5)		3.436	73.0(4)

Note. Cg is the centroid of aromatic rings, Perp is perpendicular to the plane of the ring, α is the angle between the planes of aromatic fragments.

Table S3. Hydrogen bonds in the crystal packing of complex **3**.

Interactions	Distance, Å				D – H···A, °
	D–H	Symmetry code	H···A	D···A	
O(6)–H(6)···O(8)	0.88		1.64	2.502(6)	166
C(18)–H(18)···F(3)	0.95	-1+x,3/2-y,-1/2+z	2.46	3.224(8)	137
C(21)–H(21)···F(7)	0.95		2.24	3.125(8)	155
O(28)–H(28)···O(4)	0.95	1-x,1-y,1-z	2.52	3.421(8)	159

V. Supplementary photoluminescent data

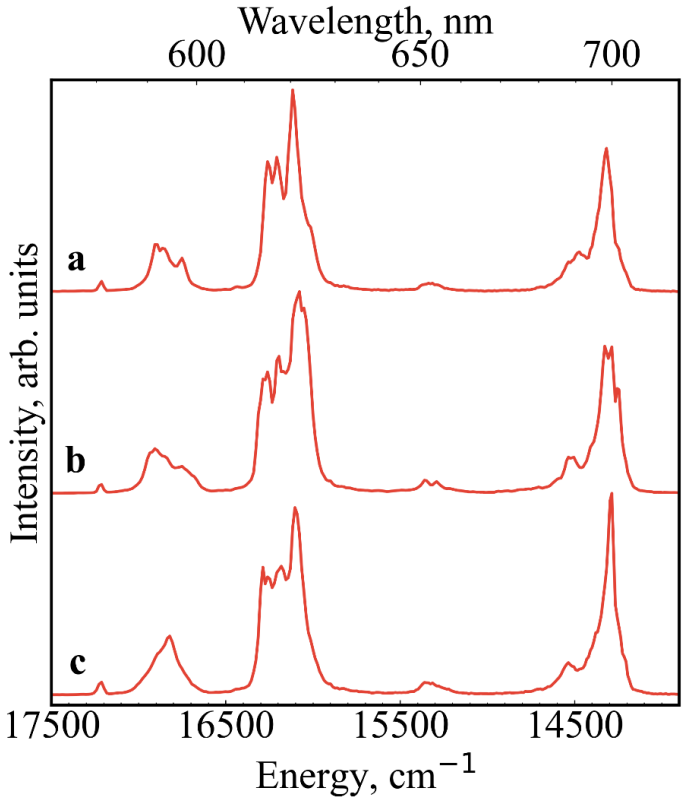


Figure S4. Photoluminescence spectra of **1** (a), **2** (b) and **3** (c) recorded at 300 K upon excitation at 280 nm.

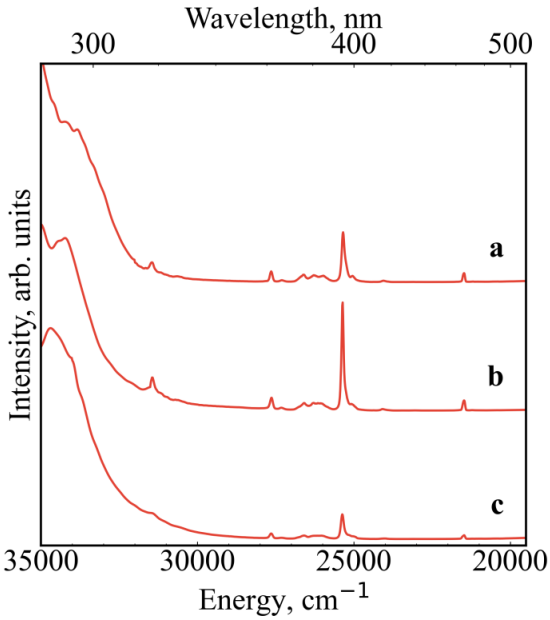


Figure S5. Photoluminescence excitation spectra of **1** (a), **2** (b) and **3** (c) recorded at 300 K with emission monitored at 615 nm.

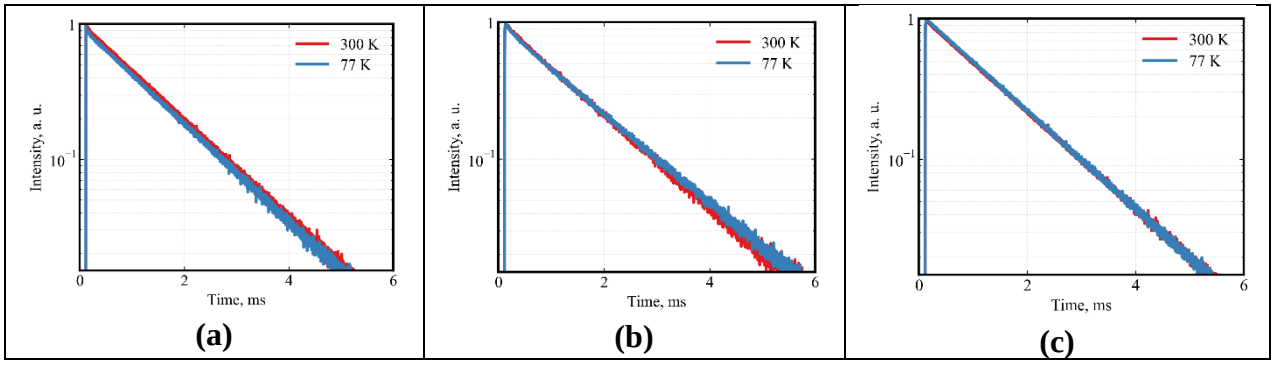


Figure S6. Luminescence decay curves of **1** (a), **2** (b) and **3** (c) recorded at 300 K and 77 K. The decays were monitored at λ_{ex} = 340 nm and λ_{em} = 615 nm

IV. References

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