## SUPPLEMENTARY INFORMATION

# Decanuclear {Cu<sup>I</sup><sub>6</sub>Re<sup>V</sup><sub>4</sub>} clusters based on cyanido and nitrido molecular bridges as efficient ligand-modulated luminophores

Michal Liberka,<sup>ab</sup> Piotr Gas,<sup>a</sup> and Szymon Chorazy\*<sup>a</sup>

<sup>a</sup>Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Poland <sup>b</sup>Doctoral School of Exact and Natural Sciences, Jagiellonian University, Łojasiewicza 11, 30-348 Kraków, Poland

\*Corresponding author: simon.chorazy@uj.edu.pl

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#### **Experimental section**

#### <u>Materials</u>

All commercially available reagents used for the syntheses of molecular precursors and reported compounds, including  $Cu^{II}(CIO_4)_2 \cdot 6H_2O$  (CAS: 10294-46-9), Cu metal (CAS: 7440–50–8), diphenyl-2-pyridylphosphine (dppy; CAS: 37943-90-1), Re<sub>2</sub>O<sub>7</sub> (CAS: 1314-68-7), triphenylphosphine (CAS: 603-35-0), hydrazine sulfate (CAS: 10034-93-2), PPh<sub>4</sub>Cl (CAS: 2001-45-8), 3-pyridinecarbonitrile (3pcn; CAS: 100-54-9), pyridine–3-carboxylic acid (3pca; CAS: 59-67-6), *trans*-3-(3-pyridyl)acrylic acid (3paa; CAS: 19337-97-4), and all necessary solvents, were purchased from Sigma Aldrich and used as received without further purification.

#### Synthesis of molecular precursors

**Synthesis of [Cu'(MeCN)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub>.** The copper(I) precursor was prepared using an adapted literature procedure.<sup>S1</sup> The Cu<sup>II</sup>(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (5 g, 0.0135 mol) starting material was dissolved in 100 mL of MeCN, then, the excess of copper metal (3.4 g, 0.054 mol) was added. The resulting reaction mixture was stirred for 4 h at room temperature. The grey solution with white suspension was filtered and the filtrate was evaporated to give white microcrystals of the [Cu<sup>I</sup>(MeCN)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> precursor which was identical to those obtained within the mentioned literature synthesis.<sup>S1</sup>

**Synthesis of [Cu<sup>1</sup><sub>2</sub>(dppy)<sub>3</sub>(MeCN)](ClO<sub>4</sub>)<sub>2</sub>.** This molecular precursor was prepared by the slight modification of the literature procedure.<sup>52</sup> The mixture of [Cu<sup>1</sup>(MeCN)<sub>4</sub>](ClO<sub>4</sub>) (393 mg, 1.2 mmol) and diphenyl-2-pyridylphosphine (dppy; 474 mg, 1.8 mmol) starting materials (the first of them prepared in the separate step, discussed above) was refluxed in 10 mL acetonitrile under inert atmosphere for 1 h. The resulting mixture was then cooled down to room temperature and filtered afterward. The filtrate was concentrated and diethyl ether was added to precipitate the [Cu<sup>1</sup><sub>2</sub>(dppy)<sub>3</sub>(MeCN)](ClO<sub>4</sub>)<sub>2</sub> precursor as a white solid, which was then separated by vacuum filtration. Slow evaporation of the crude product from the mixture of MeCN/Et<sub>2</sub>O afforded colorless crystals, whose purity was proven using a powder X-ray diffraction (P-XRD) method. This product agrees well with the result of the synthesis described in the mentioned article.<sup>52</sup>

**Synthesis of (PPh<sub>4</sub>)<sub>2</sub>[Re<sup>V</sup>(CN)<sub>4</sub>(N)]·H<sub>2</sub>O.** The preparation of the (PPh<sub>4</sub>)<sub>2</sub>[Re<sup>V</sup>(CN)<sub>4</sub>(N)]·H<sub>2</sub>O cyanido-nitrido rhenium(V) precursor, where N<sup>3-</sup> stands for the nitrido ligand, was done according to literature procedures.<sup>53,54</sup> First, the [Re<sup>V</sup>Cl<sub>2</sub>(O)(OEt)(PPh<sub>3</sub>)<sub>2</sub>] (O<sup>2-</sup> stands for the oxido ligand) neutral complex in the solid state was obtained from the perrhenic acid (prepared separately from Re<sub>2</sub>O<sub>7</sub> dissolved in concentrated hydrochloric acid) through the reaction with triphenylphosphine in absolute ethanol.<sup>53</sup> Then, the [Re<sup>V</sup>Cl<sub>2</sub>(N)(PPh<sub>3</sub>)<sub>2</sub>] precursor was obtained in the reaction of previously prepared [Re<sup>V</sup>Cl<sub>2</sub>(O)(OEt) (PPh<sub>3</sub>)<sub>2</sub>] with hydrazine sulfate in the alcoholic medium, and it was treated with potassium cyanide to form the K<sub>2</sub>[Re<sup>V</sup>(CN)<sub>4</sub>(N)]·H<sub>2</sub>O salt.<sup>54</sup> Its organic tetraphenylphosphonium salt was prepared by precipitation from the water solution using the mentioned potassium salt together with the subtle excess of PPh<sub>4</sub>Cl. As in the cases of other prepared molecular precursors, the obtained organic salt of the cyanido-nitrido Re(V) complexes was found to agree with the related published reports.<sup>54,55</sup>

#### Synthesis of compounds 1, 2, 3, and 4

#### Synthesis and basic characterization of 1

To the solution of  $(PPh_4)_2[Re^{V}(CN)_4(N)] \cdot H_2O$  (10.0 mg, 0.01 mmol) in 1 mL of MeOH, the solution of  $[Cu^{l}_2(dppy)_3](ClO_4)_2$  (11.2 mg, 0.01 mmol) in 1.1 ml of the MeOH:DMF (10:1) mixture was added. This resulted in the precipitation white-yellow solid. The mixture was closed and left undisturbed. After about one month, a large number of well-shaped yellow crystals of 1 appeared. Their composition,  $\{[Cu^{l}(dppy)]_2 [Cu^{l}(dppy)]_2 [Re^{V}(CN)_4(N)(MeOH)]_2\} \cdot 14MeOH, was defined by a single-crystal X-ray diffraction (SC-XRD) analysis. The phase purity of the obtained material was proven using a powder X-ray diffraction (P-XRD) method (Fig. S5). The crystals of 1 are stable in the mother solution or placed in diethyl ether. On the other hand, washing of these crystals with <math>Et_2O$  followed by drying in the air leads to the relatively quick removal of MeOH molecules. This results in the air-stable solvent-free phase with the composition of  $\{[Cu^{l}(dppy)]_2[Cu^{l}(dppy)_2]_4[Re^{V}(CN)_3(N)(dppy)]_2[Re^{V}(CN)_4(N)]_2\}$  (1'), as determined by the CHNS elemental analysis and thermogravimetric (TG) measurements (Fig. S1). Yield (based on Re): 5.2 mg (44%).

IR spectrum (Fig. S2, BaF<sub>2</sub>, cm<sup>-1</sup>). C=N<sup>-</sup> stretching vibrations: 2170–2100, indicating the presence of both bridging and terminal cyanido ligand modes.<sup>S6</sup> CHNS elemental analysis. Anal. Calcd. for C<sub>218</sub>H<sub>168</sub>Cu<sub>6</sub>N<sub>30</sub> P<sub>12</sub>Re<sub>4</sub> (**1'**): C, 55.64%; H, 3.60%; N, 8.93%. Found: C, 55.48%; H, 3.71%; N, 9.18%. TG (Fig. S1). Constant sample mass up to the temperature of 150 °C agrees well with the presence of solvent-free phase **1'**.

#### Synthesis and basic characterization of 2, 3, and 4

The 1 mL portion of MeOH solution containing  $(PPh_4)_2[Re^{V}(CN)_4(N)] \cdot H_2O$  (10.0 mg, 0.01 mmol) and 0.3 mmol of the appropriate ligand (L<sub>pv</sub>), i.e., 3-pyridinecarbonitrile (3pcn; 31.2 mg, 0.3 mmol) for **2**, pyridine-3carboxylic acid (3pca; 36.9 mg, 0.3 mmol) for 3, trans-3-(3-pyridyl)acrylic acid (3paa; 44.7 mg, 0.3 mmol) for 4, were added to the solution of  $[Cu_2^{1}(dppy)_3](ClO_4)_2$  (11.2 mg, 0.01 mmol) in 1.1 ml of the MeOH:DMF (10:1) mixture. This resulted in the precipitation white-yellow solid. The mixture was closed and left undisturbed. After about one month, a large number of well-shaped yellow crystals of 2, 3, or 4 appeared. Their composition,  $\{[Cu^{\dagger}(dppy)]_{2}[Cu^{\dagger}(dppy)]_{2}]_{4}[Re^{\vee}(CN)_{3}(N)(dppy)]_{2}[Re^{\vee}(CN)_{4}(N)(L_{py})_{x}(MeOH)_{1-x}]_{2}\} \cdot n MeOH (L_{py})_{x}(MeOH)_{1-x}]_{2}$ = 3pcn in 2, 3pca in 3, and 3paa in 4; x = 0.822 in 2, 1 in 3, and 0.800 in 4; n = 20 in 2, 13 in 3, and 11 in 4), were defined by a single-crystal X-ray diffraction (SC-XRD) analysis. In particular, the partial occupancies of the organic ligand in 2 and 4 were indicated by the results of the structure refinement. This analysis shows a minor contribution of the methanol solvent at this coordination position (see the Crystal structure determination section for details). The resulting detailed composition of these two compounds is here fully depicted while in the main article, the simplified formulas with the emphasized presence of related organic ligands are provided. The phase purity of obtained compounds was proven using a powder X-ray diffraction (P-XRD) method (Fig. S5). The crystals are stable in mother solutions or placed in diethyl ether; however, washing with Et<sub>2</sub>O and drying in the air lead to the relatively quick removal of MeOH molecules to reach solvent-free phase with the general composition of  $[[Cu<sup>I</sup>(dppy)]_2[Cu<sup>I</sup>(dppy)]_2]_4[Re<sup>V</sup>(CN)_3(N)(dppy)]_2[Re<sup>V</sup>(CN)_4$  $(N)(L_{pv})_{x}_{2}$  ( $L_{pv} = 3pcn \text{ in } 2'$ , 3pca in 3', and 3paa in 4'; x = 0.822 in 2', 1 in 3', and 0.800 in 4'), as determined by the CHNS elemental analysis and thermogravimetric (TG) measurements (Fig. S1). Yield (based on Re): 4.8 mg (39 %, for 2'), 4.1 mg (33 %, for 3'), and 4.5 mg (36 %, for 4').

Compound **2**. IR spectrum (Fig. S2, BaF<sub>2</sub>, cm<sup>-1</sup>). C $\equiv$ N<sup>-</sup> stretching vibrations: 2170–2100, indicating the presence of both bridging and terminal cyanido ligand modes. CHNS elemental analysis. Anal. Calcd. for C<sub>227.863</sub>H<sub>174.576</sub>Cu<sub>6</sub>N<sub>33.288</sub>P<sub>12</sub>Re<sub>4</sub> (**2'**): C, 56.12 %; H, 3.61 %; N, 9.56 %. Found: C, 56.09 %; H, 3.83 %; N, 9.50 %. TG (Fig. S1). Constant sample mass up to the temperature of 150 °C agrees with the formation of solvent-free phase **2'** in the air.

Compound **3**. IR spectrum (Fig. S2,  $BaF_2$ , cm<sup>-1</sup>). C=N<sup>-</sup> stretching vibrations: 2170–2100, indicating the presence of both bridging and terminal cyanido ligand modes. CHNS elemental analysis. Anal. Calcd. for  $C_{230}H_{178}Cu_6N_{32}O_4P_{12}Re_4$  (**3'**): C, 55.79 %; H, 3.62 %; N, 9.05 %. Found: C, 55.91 %; H, 3.61 %; N, 8.87 %. TG (Fig. S1). Constant sample mass up to the temperature of 130 °C agrees with the formation of solvent-free phase **2'** in the air.

Compound **4**. IR spectrum (Fig. S2, BaF<sub>2</sub>, cm<sup>-1</sup>). C=N<sup>-</sup> stretching vibrations: 2170–2100, indicating the presence of both bridging and terminal cyanido ligand modes. CHNS elemental analysis. Anal. Calcd. for  $C_{230.794}H_{179.194}Cu_6N_{31.599}O_{3.198}P_{12}Re_4$  (**4'**): C, 56.07 %; H, 3.65 %; N, 8.95 %. Found: C, 56.08 %; H, 3.75 %; N, 9.12 %. TG (Fig. S1). Constant sample mass up to the temperature of 150 °C agrees with the formation of solvent-free phase **2'** in the air.

#### Synthesis of reference compounds for the interpretation of optical properties of 1-4

For a detailed and more accurate interpretation of the optical properties of the obtained compounds of **1**–**4**, we additionally prepared crystalline compounds containing rhenium(V) complexes found in the crystal structures of **1**–**4** but without the combination with Cu(I) complexes. This set of reference compounds included (PPh<sub>4</sub>)[Re<sup>V</sup>(CN)<sub>3</sub>(N)(dppy)]·2MeOH·2MeCN (**Re-dppy**) as well as the series of (PPh<sub>4</sub>)<sub>2</sub> [Re<sup>V</sup>(CN)<sub>4</sub>(N)(L<sub>py</sub>)]·solvent (L<sub>py</sub> = MeOH in **Re-MeOH**, 3pcn in **Re-3pcn**, 3pca in **Re-3pca**, and 3paa in **Re-3paa**). Moreover, we also prepared the reference compound containing a Cu(I) complex with a dppy ligand but without the combination with Re(V) complexes, i.e., [Cu<sup>I</sup>(SCN)(dppy)<sub>3</sub>] (**Cu-dppy**), with only Cu–P coordination bonds and the similar geometry to tetrahedral Cu(I) complexes as present in the crystal structures of **1–4**. All the compounds were prepared through slight modifications of the literature procedures.<sup>S7-S10</sup> The compositions of obtained reference materials were defined by single-crystal X-ray diffraction (SC-XRD) analysis, while their phase purity was proven using a powder X-ray diffraction (P-XRD)

method and infrared (IR) spectroscopy (Fig. S2 and S11; Tables S7 and S8), all confronted with the related published reports confirming the proper products of the syntheses.<sup>S7–S10</sup>

**Synthesis of Re-dppy.** This reference compound was prepared by a slight modification of the literature procedure for the analogous compound.<sup>57</sup> The mixture of  $K_2[Re^{V}(CN)_4(N)] \cdot H_2O$  (0.175 mmol) and diphenyl-2-pyridylphosphine (dppy; 0.831 mmol) in 24 mL of the H<sub>2</sub>O:EtOH mixture (1:3) was refluxed overnight. The volume of the mixture was reduced, the solution was filtered, and 5 mL of the H<sub>2</sub>O solution of PPh<sub>4</sub>Cl (0.242 mmol) was added to the filtrate. The resulting orange precipitate was filtered, dissolved in MeCN, and chromatographed on a silica gel column. The residue was recrystallized from the MeOH/MeCN/Et<sub>2</sub>O mixture to give orange crystals of (PPh<sub>4</sub>)[Re<sup>V</sup>(CN)<sub>3</sub>(N)(dppy)]·3.75MeOH (**Re-dppy**).

**Synthesis of Re–MeOH.** This reference compound was prepared by the recrystallization of the  $(PPh_4)_2[Re^{V}(CN)_4(N)] \cdot H_2O$  precursor material from the MeOH/Et<sub>2</sub>O mixture to give  $(PPh_4)_2[Re^{V}(CN)_4(N)] \cdot (MeOH)] \cdot 3MeOH$  (**Re–MeOH**), as was described in the literature procedure.<sup>58</sup> This reference material was found to be identical to those described in the published report as we checked by the SC-XRD analysis (the crystal structure is not presented here as it appears in the related article).<sup>58</sup>

**Synthesis of Re–3pcn, Re–3pca, and Re–3paa.** First, the tetracyanidonitridorhenate(V) precursor of  $(PPh_4)_2[Re^{V}(CN)_4(N)]$  was prepared by a slight modification of the literature procedure for the analogous compounds.<sup>59</sup> Then, this precursor of  $(PPh_4)_2[Re^{V}(CN)_4(N)]$  (0.03 mmol) and the 0.3 mmol portion of the appropriate ligand  $(L_{py})$ , i.e., 3-pyridinecarbonitrile (3pcn) for **Re–3pcn**, pyridine-3-carboxylic acid (3pca) for **Re–3pca**, *trans*-3-(3-pyridyl)acrylic acid (3paa) for **Re–3paa**, were dissolved together in 3 mL of the MeOH:CH<sub>2</sub>Cl<sub>2</sub> mixture (1:2). After that, 7 mL of diethyl ether was layered on the respective solution. After several days yellow crystals of  $(PPh_4)_2[Re^{V}(CN)_4(N)(3pcn)]\cdot 0.45CH_2Cl_2$  (**Re–3pcn**),  $(PPh_4)_2[Re^{V}(CN)_4(N)(3pca)] \cdot MeOH$  (**Re–3pca**), and  $(PPh_4)_2[Re^{V}(CN)_4(N)(3paa)]\cdot 2MeOH$  (**Re–3paa**) appeared.<sup>59</sup>

**Synthesis of Cu–dppy.** The copper(I)-containing reference compound was prepared using the literature procedure.<sup>S10</sup> The Cu<sup>I</sup>NCS (0.5 mmol) was treated with the excess of dppy (2 mmol) dissolved in 5 mL of acetonitrile. The reflux overnight gave a white precipitate, which was filtered off. The evaporation of the filtrate gives colorless crystals of the [Cu<sup>I</sup>(SCN)(dppy)<sub>3</sub>] (**Cu–dppy**) reference material. This reference material was found to be identical to those described in the published report as we checked by the SC-XRD analysis (the crystal structure is not presented here as it appears in the related article).<sup>S10</sup>

#### **Crystal structure determination**

The single-crystal X-ray diffraction (SC-XRD) data for **1–4** were collected using a Bruker D8 Venture singlecrystal X-ray diffractometer equipped with Photon III CPAD detector, Mo K $\alpha$  (0.71073 Å) INCOATEC I $\mu$ S 3.0 microfocus sealed tube radiation source, Helios® optics, and Oxford Cryostream 800 Plus low-temperature device. Because of the easy loss of crystallization solvent molecules in contact with air and the resulting structural changes (as well as the quality of single crystals), the selected single crystals of compounds **1–4** were taken directly from the mother solution, dispersed with Apiezon N grease, and measured at 125(2) K. The absorption correction was executed using the TWINABS program.<sup>S11</sup> All crystal structures were solved by an intrinsic phasing method using SHELXT-2014/5, and refined by a full-matrix least-squares technique on  $F^2$  using the SHELXL–2018/3 program within the WinGX system.<sup>S12, S13</sup>

All non-hydrogen atoms were refined with anisotropic displacement parameters. Due to the relatively large unit cells found for the reported compounds, some reflections were affected by the beamstop. Therefore some low-order reflections have been omitted deliberately from the final least-squares refinement. Positions of hydrogen atoms within the found  $\{Cu_6^{I}Re_4^{V}\}$  coordination clusters, embedded in the structures of reported compounds, were assigned at the idealized positions and refined using a riding model with an isotropic displacement parameter set at 1.2–1.5 times  $U_{eq}$  of appropriate carrier atoms. Because of noticeable structural disorder, a considerable number of restraints of the DFIX and ISOR types (in 1, 2, 3, and 4), as well as some of the SIMU types (in 1, 2, and 4) for the selected non-hydrogen atoms in dppy ligands were applied to ensure the proper geometry and the convergence of the refinement procedure. For similar reasons, some ISOR, DFIX, and SIMU restraints were used for the 3-pyridinecarbonitrile ligand in 2 and the *trans*-3-(3-pyridyl)acrylic acid ligand in 4. Because of the large structural disorder of the organic ligands, 3pcn in 2 and 3paa in 4, these organic ligands were found in two disordered positions with partial occupancies. Moreover, the overall occupancy for the organic ligand was refined to be below 1 (0.82196 and 0.79960, for 2 and 4, respectively) as it was found necessary to consider also the coordinated solvent

molecule (methanol) with the minor but non-negligible occupancy at the same position. Only such treatment of the structural disorder in these two compounds enables the appearance of related thermal ellipsoids of satisfactory relative sizes. The alternative refinement using only two positions of the organic ligands summing to the full occupancy of 1 resulted in too large thermal ellipsoids. Therefore, it can be concluded that presumably these crystallographic positions are occupied by the methanol molecules, i.e., the organic ligands do not substitute all the methanol molecules upon going from the original clusters of 1 to compounds 2 and 4. The resulting more complex composition of the related clusters in 2 and 4 were taken into account in the experimental section in the discussion of the formula of obtained materials (see above). This effect does not happen in 3 where the full occupancy of the organic ligand without the structural disorder was found. Because of MeOH molecules of crystallization that were found to be in a noticeable disorder in 1, 2, and 4, we performed the modeling solvent disorder, and alcohol molecules were refined anisotropically with restraints on C–O bond lengths (DFIX). Moreover, some solvent atoms were in two or three alternative positions with partial occupancies, which required in individual cases additional ISOR restraints. Because of the significant structural disorder of the majority of MeOH molecules of crystallization in 2, we employed the solvent mask realized within the Olex 2 software.<sup>514</sup> Primarily we considered the part of the structure whose atoms' positions are reliable and can be reasonably refined, which includes the coordination skeleton (for all compounds). The other molecules, which consist of highly disordered MeOH molecules, were masked, thus, the further refinement was focused only on the selected non-disordered part of the structure. The compositions of highly disordered solvents were estimated based on the total residual electron density assigned to the related space of the structure, which were assigned to MeOH molecules, expected from the synthetic procedure and the comparison with the analogous compounds). Using this procedure, satisfactory refinement parameters were achieved. The reference CCDC numbers for 1, 2, 3, and 4 are 2391986, 2391987, 2391988, and 2391989, respectively. Details of crystal data and structure refinement are summarized in Table S1. The representative structural parameters are gathered in Tables S2 and S3, while the selected structural views are presented in Fig. S3 and S4. Structural figures were prepared using the Mercury 2020.3.0 software.

The crystal structures of reference materials (i.e., **Re-dppy**, **Re-3pcn**, **Re-3pca**, and **Re-3paa**) were determined, solved, and refined as for compounds **1–4**, thus with the analogous methods and treatment of the SC-XRD data as described above. The relatively large structural disorder was found in **Re-3paa** which demanded the structural refinement with two positions of the whole Re complexes with partial occupancies. The reference CCDC numbers for **Re-3pcn**, **Re-3pca**, **Re-3paa**, and **Re-dppy**, are 2391990, 2391991, 2391992, and 2391993, respectively. Details of crystal data and structure refinement are summarized in Table S7, while the related structural parameters are gathered in Table S8. The selected structural views for these reference materials are presented in Fig. S11.

The powder X-ray diffraction (P-XRD) data were collected using a Bruker D8 Advance Eco powder diffractometer equipped with a Cu K $\alpha$  (1.5419 Å) radiation source. The P-XRD measurements were conducted at room temperature for the polycrystalline samples covered by MeOH, and inserted into a glass capillary (diameter of 0.5 mm) using the appropriate experimental setup for rotating capillary (Fig. S5).

#### **Physical techniques and calculations**

For all physicochemical measurements, the crystals of **1**, **2**, **3**, and **4** compounds were thoroughly washed several times with pure methanol.

The CHNS elemental analyses were measured using an Elemental Vario Micro Cube analyzer.

The IR absorption spectra were measured on selected single crystals covered by Apiezon N grease using a Thermo Scientific Nicolet iN10 Fourier transform infrared (FTIR) spectrometer in the 4000–700 cm<sup>-1</sup> range.

The TGA curves were collected under a nitrogen atmosphere using a TG209 F1 Libra thermogravimetric analyzer with Al pans as holders. The TGA data were gathered in the 20–400 °C temperature range within the measurement executed with a heating rate of 1 °C·min<sup>-1</sup>.

The solid-state photoluminescent properties were measured using an FS5 spectrofluorometer (Edinburgh Instruments) equipped with a Xe (150 W) arc lamp as an excitation source, and a Hamamatsu photomultiplier of the R928P type as a detector. Emission lifetime measurements were conducted on the FS5 spectrofluorometer using an FS5 multichannel scaling module with a microsecond Xe flash-lamp (5 W). For all types of photoluminescent measurements, the powder samples of **1**, **2**, **3**, and **4**, were inserted in a

quartz tube and covered with methanol, while the solvent-free phases of **1**', **2**', **3**', and **4**', were thoroughly washed several times with pure methanol, dried and inserted directly in a quartz tube. Absolute luminescence quantum yields (QYs) were determined by a direct excitation method using an integrating sphere module for the FS5 spectrofluorometer and barium sulfate as reference material.<sup>S15</sup> Luminescent background corrections were performed within the Fluoracle software (Edinburgh Instruments).

Continuous Shape Measure (CShM) analyses (Tables S4 and S5) for the determination of the coordination geometries of  $Cu^{I}$  and  $Re^{V}$  complexes in **1–4** were conducted using the SHAPE software, version 2.1.<sup>S16,S17</sup>

It is worth adding here a broadened comment on the stability of the reported compounds influencing the experimental details for their physicochemical characterization. The reported compounds 1-4 were crystallized from a methanol solution (with a small addition of DMF, details in the experimental part). The crystal structures of the compounds were determined (using the SC-XRD analysis) for selected single crystals taken directly from the mother solution, and dispersed with Apiezon N grease; thus, they are stable in this protective grease. We also checked that the crystals of 1-4 are stable in mother solutions (MeOH with the small admixture of DMF) as well as placed in diethyl ether or methanol. On the other hand, we found that washing the bulk samples of 1–4 with  $Et_2O$  followed by drying in the air led to the relatively quick removal of MeOH molecules to reach solvent-free phases, which results in the loss of their singlecrystal nature (thus, the SC-XRD analyses could not be performed). For this reason, to further reliably interpret the optical data using the structural models from the SC-XRD analyses, all physicochemical studies, including spectroscopic measurements, were carried out for samples protected with MeOH. The role of the MeOH covering the investigated samples is therefore to protect the crystals from the exchange of the solvent of crystallization. In this context, the analogous results of physicochemical characterization can be obtained using the crystals covered by the Apiezon N grease or other protective grease. However, using the methanol was found to be much better as the Apiezon N grease has a yellow color and shows weak broadband blue emission, thus making the large experimental background in the optical studies. On the other hand, using the mother solution (in which the crystals are also stable) was also not ideal for optical studies as cooling can lead to the additional precipitation of the emissive material or the frozen solution can be weakly emissive. Therefore, the most reliable optical data can be gathered using the pure solvent of methanol or diethyl ether. In both of them, the crystals of the reported compounds are stable and exhibit identical optical properties. Because of the practical reasons (lower volatility), we performed all the measurements for the samples covered by the small amounts of methanol. In this solvent, the crystals of 1–4 reveal the crystal structure precisely determined by the SC-XRD analysis; thus, we can be sure that the observed optical phenomena can be reliably interpreted based on the obtained structural models. In addition, we examined the impact of the air-drying of compounds 1-4, leading to the transformation into the 1'-4' phases (desolvated ones), on their photoluminescence. The excitation/emission spectra for 1'-4' were found to be very similar in comparison to 1-4 while the solvent removal was found to mainly modify the emission lifetimes. We did not focus on these changes due to the impossibility of determining the crystal structures of the air-dried phases; however, the related data were placed in the ESI (Fig. S13 and Table S11, see below).



**Fig. S1** Thermogravimetric (TG) curves for the polycrystalline samples of **1**', **2**', **3**', and **4**' (air-dried powder forms of **1**, **2**, **3**, and **4**, respectively), collected in the temperature range 25–380 °C. The vertical lines represent the decomposition temperature of the respective compounds.

**Comment to Fig. S1:** All air-dried compounds, i.e., **1'**, **2'**, **3'**, and **4'**, are thermally stable up to about 150 °C. This proves that drying the crystals of **1–4** in the air leads to the relatively quick removal of both coordinated (in **1**) and non-coordinated (in **1–4**) MeOH molecules that result in the solvent-free phases **1'–4'**, respectively. This observation is in line with the expected mass change deduced from the CHNS elemental analysis (see Experimental section). After heating the samples to about 200 °C, there is a rapid decrease in mass, which is related to the decomposition of dppy (in **1–4**), 3paa (in **2**), 3pcn (in **3**), and 3pca (in **4**) ligands, and/or the removal of cyanido/nitrido ligands, presumably leading also to the decomposition of the compounds.



**Fig. S2** Infrared (IR) absorption spectra of the polycrystalline samples of **1**, **2**, **3**, and **4**, presented in the broad 4000–900 cm<sup>-1</sup> region (left part) and the limited 2300–2000 cm<sup>-1</sup> range (right part). The spectra in the cyanido stretching vibrations range (right part) were compared with the respective spectra of **Re–dppy**, **Re–MeOH**, **Re–3pcn**, **Re–3pca**, and **Re–3paa** reference materials. The covered part of the spectrum in the 3100–2800 cm<sup>-1</sup> range (in the left part) is related to the unusual absorption of Apiezon N grease used for the protection of the crystals. The vertical line in the right part of the figure distinguishes the higher-energy range assignable to the bridging cyanido ligands from the lower-energy part ascribable to the terminal cyanido ligands.

**Comment to Fig. S2:** The IR spectra of compounds **1–4** are very similar to each other. The extensive areas of absorption bands in the 1800–700 cm<sup>-1</sup> range are associated with the skeletal vibrations of dppy (in **1–4**), as well as 3paa (in **2**), 3pcn (in **3**), and 3pca (in **4**) ligands. Above 2800 cm<sup>-1</sup>, v(O–H) ring absorption bands associated with coordinated (in **1**) and non-coordinated methanol molecules, and the carboxyl groups (in **3** and **4**), as well as v(C–H) ring vibrations are detected. In the 2300–2000 cm<sup>-1</sup> range, the characteristic peaks related to the stretching vibrations of C=N<sup>-</sup> groups are observed. The higher energy bands above 2250 cm<sup>-1</sup> in **2** can be assigned to the nitrile group of the 3paa ligand, while a set of peaks below 2170 cm<sup>-1</sup> is related to cyanido ligands. Compared to the **Re–dppy**, **Re–MeOH**, **Re–3pcn**, **Re–3pca**, and **Re–3paa** reference materials, the cyanido ligand stretching vibrations in **1–4** appear within a slightly broader range covered by a few overlapping peaks. This range can be divided into the part related to the terminal cyanido ligands, represented by IR peaks of the 2140–2100 cm<sup>-1</sup> range, and the higher energy part ascribable to the bridging -C=N- groups, which is observed in 2170–2140 cm<sup>-1</sup> region in the presented compounds, while being absent in the reference compounds. This interpretation stays in good agreement with the structural data and literature.<sup>53–59</sup>

 Table S1 Crystal data and structure refinement parameters for 1–4.

compound	1	2	3	4						
formula	$\begin{array}{c} C_{234}H_{234}Cu_6 \\ N_{30}O_{16}P_{12}Re_4 \end{array}$	$\begin{array}{c} C_{228.22}H_{176}Cu_6\\ N_{33.29}O_{0.36}P_{12}Re_4 \end{array}$	$\begin{array}{c} C_{243}H_{230}Cu_6 \\ N_{32}O_{17}P_{12}Re_4 \end{array}$	$\begin{array}{c} C_{242.2}H_{224.8}Cu_6\\ N_{31.6}O_{14.6}P_{12}Re_4 \end{array}$						
formula weight / g·mol⁻¹	5218.29	4888.17	5368.38	5309.46						
Т/К		125	5(2)							
λ / Å		0.71073 (Μο Κα)								
crystal system		tric	linic							
space group		P1 (No. 2)								
a / Å	17.7996(17)	17.8262(18)	17.501(2)	17.8452(19)						
b / Å	19.2840(18)	19.473(2)	18.190(3)	19.7115(19)						
c / Å	21.9051(19)	21.915(2)	22.250(3)	21.973(2)						
lpha / deg	111.005(3)	111.371(3)	71.562(5)	111.983(3)						
<i>в</i> / deg	99.500(3)	99.586(3)	72.401(5)	99.066(3)						
γ/deg	110.975(3)	110.633(3)	62.918(5)	110.968(3)						
V / Å <sup>3</sup>	6171.8(10)	6238.6(11)	5876.5(14)	6301.8(11)						
Z	1	1	1	1						
calculated density / g·cm <sup>-3</sup>	1.404	1.298	1.517	1.399						
absorption coefficient / cm <sup>-1</sup>	2.599	2.561	2.732	2.546						
F(000)	2598	2435	2702	2670						
Θ range / °	1.986-25.350	1.906-25.027	1.964–25.027	1.895-25.026						
limiting indices	-21 < h < 21 -23 < k < 23 -26 < l < 26	-21 < h < 21 -23 < k < 23 -26 < l < 26	-20 < h < 20 -21 < k < 21 -26 < l < 26	-21 < h < 21 -21 < k < 23 -26 < l < 26						
collected reflections	111362	60151	57204	58620						
R <sub>int</sub>	0.0758	0.0804	0.0893	0.0879						
completeness	0.999	0.999	0.999	0.999						
data/restraints/parameters	22601/462/1607	22016/354/1339	20736/272/1532	22245/414/1584						
GOF on <i>F</i> <sup>2</sup>	1.042	1.006	1.006	1.018						
final <i>R</i> indices	$R_1 = 0.0431$ [/>2 $\sigma$ (/)] $wR_2 = 0.1198$ (all data)	$R_1 = 0.0501$ [/>2 $\sigma$ (/)] $wR_2 = 0.1179$ (all data)	$R_1 = 0.0545$ [/>2 $\sigma$ (/)] $wR_2 = 0.1235$ (all data)	$R_1 = 0.0649$ [/>2 $\sigma$ (/)] $wR_2 = 0.1759$ (all data)						
largest diffraction peak and hole / e·Å⁻³	1.077 and –0.844	1.445 and -0.765	1.023 and –0.876	1.305 and –0.913						



**Fig. S3** Detailed structural views of compound **1**: the views of the whole supramolecular network, comprising coordination clusters and methanol molecules of crystallization, presented along the main *a*, *b*, and *c* crystallographic axes (a), the enlarged view of a decanuclear { $Cu_6^{1}Re_4^{V}$ } cluster (b), detailed views of the coordination spheres of intracluster  $Cu^{1}$  and  $Re^{V}$  centers (c), the asymmetric unit with the labeling scheme for symmetrically independent metal centers, and with the naming of used ligands and solvent (d), and detailed view of the coordination skeleton of { $Cu_6^{1}Re_4^{V}$ } clusters (e). Thermal ellipsoids for the asymmetric unit are presented in (d) at the 50% probability level. Hydrogen atoms in the (b) and (e) parts, as well as dppy ligands coordinated to  $Cu^{1}$  centers, in the (e) part, were omitted for clarity. Related detailed structural parameters are presented in Table S2.



**Fig. S4** (part 1/2) Detailed structural views of **2**, **3**, and **4**: the enlarged view of  $\{Cu_6^{l}Re_4^{V}\}$  clusters in **2**, **3**, and **4** (a, b, and c, respectively; the parts representing the main differences between the compounds are indicated by a colored background), detailed views of the coordination spheres of intracluster  $Cu^{l}$  and  $Re^{V}$  centers (d) and (e, the structures of the ligands also added), detailed views of the coordination skeletons of  $\{Cu_6^{l}Re_4^{V}\}$  clusters with organic ligands indicated (f), and the asymmetric units with the labeling schemes for symmetrically independent metal centers and the indications of dppy ligands and solvents (g). Thermal ellipsoids for the asymmetric unit are presented in (g) at the 50% probability level. H-atoms in the (a–c) and (f) parts, as well as dppy ligands coordinated to  $Cu^{l}$  centers, in the (f) part, were omitted for clarity. Related structural parameters are presented in Table S2. **2** and **4** reveal a significant disorder in the position of the organic ligand and a single additional position of a coordinated methanol molecule, all with partial occupancies summing to 1. In the (g) part, all the related atoms are presented while in the other parts, only the atoms related to the position of the highest occupancies are shown. They belong to the organic ligand while a methanol molecule represents only the minor occupancy (ca. 0.2 and below), thus this position is dominantly occupied by the organic ligand (exclusively by the organic ligand in the case of **3**).



**Fig. S4** (part 2/2) Detailed structural views of **2**, **3**, and **4**: the enlarged view of { $Cu_{6}^{1}Re_{4}^{V}$ } clusters in **2**, **3**, and **4** (a, b, and c, respectively; the parts representing the main differences between the compounds are indicated by a colored background), detailed views of the coordination spheres of intracluster  $Cu^{1}$  and  $Re^{V}$  centers (d) and (e, the structures of the ligands also added), detailed views of the coordination skeletons of { $Cu_{6}^{1}Re_{4}^{V}$ } clusters with organic ligands indicated (f), and the asymmetric units with the labeling schemes for symmetrically independent metal centers and the indications of dppy ligands and solvents (g). Thermal ellipsoids for the asymmetric unit are presented in (g) at the 50% probability level. H-atoms in the (a–c) and (f) parts, as well as dppy ligands coordinated to  $Cu^{1}$  centers, in the (f) part, were omitted for clarity. Related structural parameters are presented in Table S2. **2** and **4** reveal a significant disorder in the position of the organic ligand and a single additional position of a coordinated methanol molecule, all with partial occupancies summing to 1. In the (g) part, all the related atoms are presented while in the other parts, only the atoms related to the position of the highest occupancies are shown. They belong to the organic ligand while a methanol molecule represents only the minor occupancy (ca. 0.2 and below), thus this position is dominantly occupied by the organic ligand (exclusively by the organic ligand in the case of **3**).

compound	1	2	3	4						
complex		[Cu1 <sup>ι</sup> (μ–NC)	₂(μ−N)(dppy)] <sup>4−</sup>							
Cu1–N2 / Å	2.025(5)	2.005(5)	1.999(7)	2.015(8)						
Cu1–N6 / Å	1.988(5)	1.983(5)	1.967(6)	1.992(8)						
Cu1–N7 / Å	2.014(4)	2.007(5)	2.011(6)	1.995(8)						
Cu1–P2 / Å	2.2381(15)	2.2389(19)	2.235(2)	2.241(3)						
N2–Cu1–N6 / °	101.26(18)	101.7(2)	103.6(2)	102.3(3)						
N2–Cu1–N7 / °	101.96(18)	103.0(2)	103.9(3)	103.0(3)						
N2–Cu1–P2 / °	113.54(13)	114.06(15)	112.64(19)	114.2(2)						
N6-Cu1-N7 / °	103.92(18)	102.7(2)	102.8(2)	100.6(3)						
N6-Cu1-P2 / °	115.13(13) 114.63(15)		115.70(18)	115.6(2)						
N7–Cu1–P2 / °	118.77(14)	118.59(16)	116.63(18)	118.8(3)						
complex	[Cu2 <sup>1</sup> (µ–NC) <sub>2</sub> (dppy) <sub>2</sub> ] <sup>2–</sup>									
Cu2–N3 / Å	2.023(5)	2.019(6)	2.055(7)	2.054(9)						
Cu2–N8 / Å	1.981(5)	1.994(5)	2.009(6)	2.001(7)						
Cu2–P3 / Å	2.2631(18)	2.264(2)	2.293(2)	2.267(3)						
Cu2–P4 / Å	2.182(4)/ 2.545(9)	2.262(2)	2.278(2)	2.264(3)						
N3–Cu2–N8 / °	102.2(2)	101.7(2)	101.6(2)	101.9(3))						
N3–Cu2–P3 / °	119.81(16)	119.42(16)	101.49(18)	119.4(2)						
N3–Cu2–P4 / °	102.69(19)/ 113.2(3)	104.35(17)	120.04(19)	104.9(2)						
N8–Cu2–P3 / °	112.63(14)	113.61(16)	106.41(18)	113.6(2)						
N8–Cu2–P4 / °	108.77(17)/ 95.5(2)	106.83(17)	114.69(19)	106.6(2)						
P3–Cu2–P4 / °	109.86(10)/ 110.5(2)	109.81(8)	110.98(8)	109.36(11)						
complex		[Cu3 <sup>I</sup> (µ–NC)	(µ–N)(dppy) <sub>2</sub> ] <sup>3-</sup>							
Cu3–N1 / Å	1.985(5)	2.008(6)	2.002(6)	2.000(8)						
Cu3–N9 / Å	1.985(5)	1.988(6)	2.002(6)	1.981(8)						
Cu3–P5 / Å	2.2512(17)	2.265(2)	2.248(2)	2.254(3)						
Cu3–P6 / Å	2.2690(17)	2.246(2)	2.263(2)	2.265(3)						
N1–Cu3–N9 / °	101.70(19)	100.6(2)	101.1(2)	99.9(3)						
N1-Cu3-P5 / °	115.57(14)	98.61(16)	116.86(18)	116.7(2)						
N1-Cu3-P6 / °	98.17(14)	116.04(16)	100.26(18)	98.2(2)						
N9–Cu3–P5 / °	116.06(15)	107.74(17)	116.25(19)	115.9(3)						
N9–Cu3–P6 / °	107.73(15)	116.13(16)	107.41(18)	107.5(2)						
P5–Cu3–P6 / °	115.37(6)	115.40(8)	113.12(8)	116.13(11)						

### **Table S2** (part 1/2) Detailed crystal structure parameters of Cu<sup>1</sup> and Re<sup>v</sup> complexes in **1–4**.

compound	1	2	3	4	
complex		<i>mer</i> –[Re1 <sup>∨</sup> (µ−Cf	N)₃(µ−N)(dppy)]⁻		
Re1–C / Å	2.096(6)-2.107(7)	2.091(7)-2.107(7)	2.099(8)-2.110(8)	2.097(1)-2.114(1)	
Re1≡N1 / Å	1.672(5)	1.655(6)	1.658(6)	1.660(8)	
Re1–N5 / Å	2.416(5)	2.422(6)	2.409(6)	2.420(9)	
Re1–P1 / Å	2.4215(15	2.4198(18)	2.426(2)	2.426(3)	
C2–Re1–C3 / °	85.1(2)	85.3(2)	85.6(3)	84.5(4)	
C2–Re1–C4 / °	161.8(2)	162.3(3)	162.7(3)	162.3(4)	
C2–Re1≡N1/°	97.3(2)	96.9(2)	96.3(3)	97.2(3)	
C2–Re1–N5 / °	83.30(19)	83.9(2)	84.3(2)	83.7(3)	
C2-Re1-P1/°	91.17(14)	91.76(17)	91.8(2)	92.0(3)	
C3–Re1–C4 / °	84.8(2)	84.7(2)	85.3(3)	84.7(4)	
C3–Re1≡N1/°	107.4(2)	107.8(3)	106.8(3)	107.8(4)	
C3–Re1–N5 / °	92.6(2)	92.5(2)	93.2(2)	92.8(3)	
C3-Re1-P1/°	155.98(18)	156.04(18)	156.5(2)	156.1(3)	
C4–Re1≡N1/°	100.2(2)	100.1(3)	100.5(3)	99.4(4)	
C4–Re1–N5 / °	82.1(2)	82.0(2)	81.5(2)	82.9(3)	
C4–Re1–P1/°	91.87(16)	91.43(19)	90.7(2)	92.2(3)	
N1=Re1-N5 / °	160.00(19)	159.7(2)	160.0(3)	159.3(3)	
N1=Re1-P1/°	96.61(16)	96.12(19)	96.8(2)	96.0(3)	
N5-Re1-P1/°	63.39(12)	63.57(14)	63.21(16)	63.3(2)	
complex		<i>trans</i> −[Re2 <sup>∨</sup> (μ−	CN)4(µ-N)(L)] <sup>2-</sup>		
L	MeOH	3pcn	Зрса	Зраа	
Re2–C/ Å	2.090(5)-2.118(6)	2.088(7)-2.116(7)	2.083(8)-2.121(8)	2.083(1)-2.102(9)	
Re2≡N6 / Å	1.670(5)	1.678(5)	1.672(6)	1.656(8)	
Re2–L / Å	2.357(4)	2.436(7)/2.441(6)	2.430(6)	2.437(8)/ 2.444(9)	
C–Re2–C ( <i>cis</i> ) / °	86.1(2)-93.9(2)	85.7(2)-94.4(2)	86.9(3)-94.3(3)	86.4(4)-94.3(4)	
C–Re2–C ( <i>trans</i> ) / °	162.4(2), 165.3(2)	161.6(2), 165.9(3)	161.8(3), 167.2(3)	161.7(4), 167.5(4)	
C–Re2≡N6 / °	94.3(2)-100.5(2)	93.7(2)-101.2(2)	94.0(3)-101.8(3)	93.8(4)-101.6(4)	
C–Re2–L/°	81.2(2)-83.3(2)	78.7(2)-83.4(2)x	79.5(2)-84.5(2)	79.2(3)-84.7(4)	
N6=Re2-L/°	177.03(18)	170.5(4)/173.8(5)	174.8(2)	170.9(5)/172.8(7)	

**Table S2** (part 2/2) Detailed crystal structure parameters of  $Cu^{I}$  and  $Re^{V}$  complexes in 1–4.

**Table S3** Comparison of selected distances and angles between  $Cu^{I}$  and  $Re^{V}$  metal centers, as well as other metal-involved metric parameters, within { $Cu^{I}_{6}Re^{V}_{4}$ } clusters in the crystal structures of **1**, **2**, **3**, and **4**.

compound	1	2	3	4
Re1…Cu1/Å	5.238	5.246	5.230	5.244
Re1…Cu2 / Å	5.184	5.191	5.252	5.200
Re1…Cu3 / Å	3.647	3.652	3.648	3.649
Re2…Cu1/Å	3.633/5.228	3.633/5.224	3.607/5.222	3.620/5.216
Re2…Cu2 / Å	5.200	5.222	5.262	5.225
Re2…Cu3 / Å	5.196	5.194	5.222	5.202
Re1…Re2 / Å	6.433/7.764	6.438/7.788	6.506/7.831	6.441/7.784
Re1…Re1 / Å	12.618	12.661	12.796	12.698
Re2…Re2 / Å	6.643	6.626	6.600	6.548
Cu1…Cu1 / Å	6.078	6.089	6.083	6.144
Cu1…Cu2 / Å	6.742/7.252	6.730/7.289	6.788/7.314	6.731/7.308
Cu1…Cu3 / Å	6.284/7.880	6.287/7.908	6.213/7.927	6.277/7.952
Cu2…Cu2 / Å	12.616	12.640	12.734	12.637
Cu2…Cu3 / Å	7.575/10.262	7.603/10.277	7.522/10.365	7.608/10.282
Cu3…Cu3 / Å	12.894	12.925	12.880	12.943
Re1…Cu1…Re2 / °	91.14/95.78	91.10/96.12	92.98/97.06	91.32/96.16
Re1…Cu2…Re2/°	96.79	96.82	96.29	96.60
Re1…Cu3…Re2/°	91.65	91.71	92.61	91.67
Re2…Cu1…Re2 / °	95.43	95.16	94.99	93.89
Cu1…Re1…Cu2 / °	80.62	80.30	80.73	80.25
Cu1…Re1…Cu3 / °	88.13	88.01	86.90	87.88
Cu1…Re2…Cu1/°	84.57	84.84	85.01	86.11
Cu1…Re2…Cu2 / °	80.57/109.07	80.21/109.50	80.71/109.70	80.28/110.10
Cu1…Re2…Cu3 / °	88.93/98.23	89.01/98.76	87.44/98.75	88.85/99.51
Cu2…Re1…Cu3 / °	117.08	117.51	114.18	117.49
Cu2…Re2…Cu3 / °	161.65	161.20	162.66	160.93
Cu1–N2≡C2 / °	171.14	171.60	174.83	171.62
Cu1–N7≡C7 / °	166.60	166.53	167.93	166.82
Cu1–N6=Re2 / °	166.88	165.84	164.85	165.74
Cu2–N3≡C3 / °	160.25	161.03	163.60	161.02
Cu2–N8≡C8 / °	169.65	171.73	174.27	171.49
Cu3–N9≡C9 / °	164.89	165.98	165.46	166.65
Cu3–N1≡Re1/°	171.46	170.83	170.85	171.06

Table S4 Results of Continuous Shape Measure (CShM) analysis for four-coordinated Cu<sup>I</sup> complexes in 1–4.

CShM parameters	1	2	3	4					
geometries*	[Cu1 <sup>1</sup> (µ–NC) <sub>2</sub> (µ–N)(dppy)] <sup>4–</sup>								
SP-4	33.035	32.916	32.924	32.592					
T-4	0.989	1.006	0.860	1.089					
SS-4	7.766	7.766 7.785 8.117							
-	[Cu2 <sup>1</sup> (µ–NC) <sub>2</sub> (dppy) <sub>2</sub> ] <sup>2–</sup>								
SP-4	29.554/30.392	30.554	30.414	30.648					
T-4	0.820/1.566	0.794	0.897	0.732					
SS-4	7.193/8.758	7.621	7.522	7.508					
-		[Cu3 <sup>I</sup> (µ–NC)(µ	ι−N)(dppy)₂] <sup>3−</sup>						
SP-4	31.574	31.337	31.189	31.243					
T-4	1.113	1.097	0.945	1.238					
SS-4	8.157	8.266	8.558	8.142					

\*Continuous Shape Measure (CShM) Parameters: SP-4 - the parameter related to the square ( $D_{4h}$ ), T-4 - the parameter related to the tetrahedron ( $T_d$ ), SS-4 - the parameter related to the seesaw/sawhorse ( $C_{2v}$ ).<sup>S16,S17</sup> Continuous Shape Measure (CShM) parameter represents the distortion from ideal geometry. It equals 0 for an ideal polyhedron and increases with the increasing distortion.

Table S5 Results of Continuous Shape Measure analysis for six-coordinated Re<sup>V</sup> complexes in 1–4.

CShM parameters	1	2	3	4					
geometries*	<i>mer</i> −[Re1 <sup>v</sup> (μ−CN) <sub>3</sub> (μ−N)(dppy)] <sup>-</sup>								
HP-6	HP-6 31.286 31.384 31.011								
PPY-6	24.860	24.987	24.930	24.792					
OC-6	1.997	2.013	1.984	2.100					
TPR-6	13.857	13.834	14.099	13.680					
-	trans–[Re2 <sup>V</sup> ( $\mu$ –CN) <sub>4</sub> ( $\mu$ –N)(L)] <sup>2–</sup>								
L	MeOH	3pcn	Зрса	Зраа					
HP-6	31.882	31.332/30.762/ 32.044	32.655	30.900/32.858/ 32.020					
PPY-6	27.082	27.340/27.540/ 26.020	26.659	27.539/26.628/ 26.056					
OC-6	0.472	0.687/0.605/ 0.728	0.568	0.559/0.668/ 0.741					
TPR-6	15.289	15.360/15.316/ 13.744	14.274	13.442/14.685/ 15.477					

\*Continuous Shape Measure (CShM) Parameters: HP–6 - the parameter related to the hexagon ( $D_{6h}$ ), PPY–6 - the parameter related to the pentagonal pyramid ( $C_{5v}$ ), OC–6 - the parameter related to the octahedron ( $O_h$ ), TPR–6 - the parameter related to the trigonal prism ( $D_{3h}$ ).<sup>S16,S17</sup> Continuous Shape Measure (CShM) parameter represents the distortion from ideal geometry. It equals 0 for an ideal polyhedron and increases with the increasing distortion.



**Fig. S5** The powder X-ray diffraction (PXRD) patterns of **1**, **2**, **3**, and **4**, presented in the broad 2 $\Theta$  range of 3–30 ° (left part) and the limited low-angle region of 3.5–10° (right part). The experimental data (T = 300 K, indicated by "exp.") were compared with the patterns calculated from the respective structural models obtained from the single-crystal X-ray diffraction (SC-XRD) structural analysis (T = 100 K, indicated by "theo.").



**Fig. S6** Room-temperature solid-state UV-vis absorption spectra of the polycrystalline samples of **1–4**, gathered in the 200–700 nm range.



**Fig. S7** Detailed characteristics of solid-state photoluminescent properties of **1**, including excitation and emission spectra (a, c, and e) as well as emission decay profiles (b, d, and f) under the indicated excitation and emission wavelengths at 300 K (a, b) and 77 K (c–f), together with emission colors presented on the CIE 1931 chromaticity diagram (g). For the emission decay profiles, the mono-exponential fitting was applied, and the related best-fit curve is illustrated by a solid line in the (b), (d), and (f) parts. The related spectroscopic and CIE 1931 chromaticity parameters, as well as the best-fit parameters for the emission decay profiles, are gathered in Table S6.



**Fig. S8** Detailed characteristics of solid-state photoluminescent properties of **2**, including excitation and emission spectra (a, c, and e) as well as emission decay profiles (b, d, and f) under the indicated excitation and emission wavelengths at 300 K (a, b) and 77 K (c–f), together with emission colors presented on the CIE 1931 chromaticity diagram (g). For the emission decay profiles, the mono-exponential fitting was applied, and the related best-fit curve is illustrated by a solid line in the (b), (d), and (f) parts. The related spectroscopic and CIE 1931 chromaticity parameters, as well as the best-fit parameters for the emission decay profiles, are gathered in Table S6.



**Fig. S9** Detailed characteristics of solid-state photoluminescent properties of **3**, including excitation and emission spectra (a, c, and e) as well as emission decay profiles (b, d, and f) under the indicated excitation and emission wavelengths at 300 K (a, b) and 77 K (c–f), together with emission colors presented on the CIE 1931 chromaticity diagram (g). For the emission decay profiles, the mono-exponential fitting was applied, and the related best-fit curve is illustrated by a solid line in the (b), (d), and (f) parts. The related spectroscopic and CIE 1931 chromaticity parameters, as well as the best-fit parameters for the emission decay profiles, are gathered in Table S6.



**Fig. S10** Detailed characteristics of solid-state photoluminescent properties of **4**, including excitation and emission spectra (a, c, and e) as well as emission decay profiles (b, d, and f) under the indicated excitation and emission wavelengths at 300 K (a, b) and 77 K (c–f), together with emission colors presented on the CIE 1931 chromaticity diagram (g). For the emission decay profiles, the mono-exponential fitting was applied, and the related best-fit curve is illustrated by a solid line in the (b), (d), and (f) parts. The related spectroscopic and CIE 1931 chromaticity parameters, as well as the best-fit parameters for the emission decay profiles, are gathered in Table S6.

#### Additional comment to Fig. S7–S10 on the Cu(I) emission and the Cu(I)-to-Re(V) energy transfer in 1–4

In general, as presented in Fig. 2 and 3, as well as Fig. S7–S10, the Cu(I) to Re(V) energy transfer in the reported cluster compounds occurs both at room temperature as well as low temperature.

At RT, the high-energy excitation bands in 1-4 coincide with those in Cu(I)-dppy reference whose yellow PL was not found in 1-4. This suggests the energy transfer (ET) from Cu(I) to Re(V). Upon the lower-energy excitation (above ca. 350 nm), the same emission spectra are observed but this represents the selective excitation of Re(V) complexes as the Cu(I) complexes do not absorb light in this range.

On the contrary, at LT (77 K), upon the 290 nm excitation, **1–4** exhibit the rich emission containing both components from Re(V) and Cu(I) complexes, while, upon the 430 nm excitation, only Re(V) units provide the PL (similarly to the RT spectra). This corresponds mainly to the selective excitation of Re(V) centers by lower-energy excitation, omitting the excited levels of Cu(I) centers, while the partial Cu(I)-to-Re(V) ET plays a role in the deeper excitation.

Therefore, both at high and low temperatures, the Cu(I)-to-Re(V) energy transfer (occurring for the high energy excitation below 350 nm) can be postulated. But, at low temperatures, the remaining Cu(I) emission is strong enough to provide the valuable second emission component modifying the whole emission pattern. One can consider why the distinct residual Cu(I) emission is detectable only at low temperatures. There are a few different reasons for this, at least the two following. First, the Cu(I) emissive state increases its energy on cooling as visualized by the results for Cu(I)-dppy reference. As a result, at LT, the energy gap between the emissive state of Cu(I) complexes and Re(V) complexes increases, which leads to the lower efficiency of the related ET. Second, the residual Cu(I) emission can be present as the number of Cu(I) sites in the cluster is higher than Re(V) complexes. It might be very weak at RT being, however, greatly enhanced at LT due to the deactivation of the emission quenching pathways.

Therefore, the dual Cu(I) and Re(V) emission at LT can be postulated for the reported series of compounds. This scenario is not distinctly changed taking into account the two possibly co-existing contributions, MC and MLCT, to the emission of Re(V) complexes as in both cases the Cu(I)-to-Re(V) ET can operate (through space and/or molecular cyanido bridges).

**Table S6** Selected spectroscopic parameters of the solid-state photoluminescent properties of compounds **1**, **2**, **3**, and **4** for indicated excitation wavelengths ( $\lambda_{exc}$ ) at 300 and 77 K, including emission pattern maxima ( $\lambda_{em}^{max}$ ), the CIE 1931 chromaticity x and y parameters, absolute quantum yield ( $\Phi_{em}$ , room-temperature value only), best-fit parameters for the emission decay profiles to the mono-exponential decay function, as well as radiative ( $k_r$ ) and nonradiative ( $k_{nr}$ ) decay rate constant for the relaxation of the emissive state.

comp.	т/к	λ <sub>exc</sub> / nm	λ <sub>em</sub> <sup>max</sup> / nm	energy diff. <sup>c</sup> /	energy ch diff.°/ $\phi_{em}$ p		CIE 1931 chromaticity parameters		lifetime	decay rate constant <sup>a</sup> / 10 <sup>4</sup> s <sup>-1</sup>			
				Cm⁻¹		x	у	τ / μs	χ²	<i>k</i> r	<i>k</i> nr		
	300 <sup>b</sup>	430	590	_	0.56	0.516	0.478	12.2 ( <u>+</u> 0.13)	1.094	4.59	3.61		
1		430	507 <i>,</i> <u>535</u> , 560	1032.3	_	0.401	0.551	74.0 ( <u>+</u> 2.53)	1.083	_	-		
	77	200	450	-	-	0.269	0 220	220.0 ( <u>+</u> 2.59)	1.086	-	-		
		290	600	-	-	0.208	0.339	73.9 ( <u>±</u> 0.68)	1.014	-	-		
	300 <sup>b</sup>	430	600	-	0.72	0.539	0.457	18.1 ( <u>±</u> 0.03)	1.079	3.98	1.55		
2		430	530, 563, <u>595</u>	1105.9	-	0.501	0.473	89.2 ( <u>+</u> 0.97)	1.096	-	-		
	77	200	475	-	-	0.262	0 226	225.0 ( <u>+</u> 3.12)	1.064	-	Ι		
		230	630	-	-	0.202	0.000	89.3 (±1.01)	1.033	-	-		
	300 <sup>b</sup>	430	595	-	0.75	0.523	0.470	32.4 ( <u>+</u> 0.11)	1.036	2.31	0.77		
3		430	568, <u>600</u> , 620	939.0	-	0.569	0.429	151.8 ( <u>+</u> 0.25)	1.005	-	-		
	77	200	475	-	-	0 2 2 1	0 /11	219.8 ( <u>+</u> 2.69)	1.083	-	-		
		290	650	-	-	0.521	0.411	151.9 ( <u>+</u> 0.29)	1.050	-	-		
	300 <sup>b</sup>	430	595	-	0.84	0.535	0.461	27.1 ( <u>±</u> 0.24)	1.054	3.10	0.59		
4				430	570, <u>595</u> , 620	737.1	-	0.548	0.448	135.4 ( <u>+</u> 0.92)	1.035	-	-
	77	77	475	-	-	0.216	0 271	228.5 ( <u>±</u> 5.26)	1.081	-	-		
		290	650	_	-	0.310	0.371	136.4 (±1.47)	1.028	-	-		

<sup>a</sup>Radiative ( $k_r$ ) and nonradiative ( $k_{nr}$ ) decay rate constant for the relaxation of the emissive state are based on the relationship  $k_r = \Phi_{em}/\tau$  and  $\Phi_{em} = k_r/(k_r+k_{nr})$  in which  $\tau$  values are the luminescence lifetime and the  $\Phi_{em}$  is the quantum yield.<sup>S9 b</sup>The spectroscopic parameters for the PL properties at 300 K were presented only for the representative 430 nm excitation. The almost identical parameters for this temperature are observed for other excitation wavelengths, including the 290 nm excitation (for which the related parameters change distinctly upon cooling, see Fig. S7–S10). <sup>c</sup>The energy difference between the two highest-energy peaks of the vibronic progression which corresponds to the Re=N stretching vibration of Re(V) complexes. Table S7 Crystal data and structure refinement parameters for Re–dppy, Re–3pcn, Re–3pca, and Re–3paa reference compounds.

compound	Re-dppy	Re–3pcn	Re–3pca	Re-3paa							
formula	$C_{44}H_{34}N_5P_2Re_1$	$\begin{array}{c} C_{58.45}H_{44.90} \\ CI_{0.90}N_7P_2Re_1 \end{array}$	$C_{59}H_{49}N_6O_3P_2$ Re <sub>1</sub>	$C_{62}H_{54}N_6O_4P_2Re_1$							
formula weight / g·mol⁻¹	880.91	1125.36	1138.19	1195.26							
Т/К											
λ / Å		0.71073	(Μο Κα)								
crystal system		monoclinic									
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>P c</i> (No. 7)	P 21 (No. 4)							
a / Å	17.768(2)	8.7303(8)	8.3360(7)	13.4644(19)							
b / Å	9.5496(10)	54.337(6)	14.4518(13)	17.279(3)							
c / Å	27.529(3)	21.586(2)	21.376(2)	13.820(3)							
α / deg	90	90	90	90							
<i>в</i> / deg	102.419(3)	92.476(3)	91.822(3)	119.085(4)							
γ/deg	90	90	90	90							
V / Å <sup>3</sup>	4561.9(9)	10230.6(18)	2573.9(4)	2809.7(8)							
Z	4	8	2	2							
calculated density / g·cm <sup>-3</sup>	1.287	1.461	1.469	1.413							
absorption coefficient / cm <sup>-1</sup>	2.766	2.531	2.474	2.272							
F(000)	1752	4519	1148	1210							
Θ range / °	2.107-25.027	1.925-25.048	2.371-25.027	2.057-25.023							
limiting indices	-21 < h < 21 -10 < k < 11 -32 < l < 32	-10 < h < 9 -64 < k < 64 -25 < l < 25	-9 < h < 9 -17 < k < 17 -25 < l < 25	-16 < h < 16 -20 < k < 20 -16 < l < 16							
collected reflections	49288	118548	33089	27983							
R <sub>int</sub>	0.0892	0.0931	0.0834	0.0859							
completeness	0.999	0.997	0.998	0.999							
data/restraints/parameters	8032/72/469	18076/220/1504	8641/45/644	9804/643/735							
GOF on <i>F</i> <sup>2</sup>	1.023	1.083	0.968	1.054							
Flack parameter	-	-	0.001(6)	0.079 (6)							
final R indices	$R_1 = 0.0685$ [/>2 $\sigma$ (/)] $wR_2 = 0.1643$ (all data)	$R_1 = 0.0608$ [/>2 $\sigma$ (/)] $wR_2 = 0.1174$ (all data)	$R_1 = 0.0379$ [/>2 $\sigma$ (/)] $wR_2 = 0.0724$ (all data)	$R_1 = 0.0889$ [/>2 $\sigma$ (/)] $wR_2 = 0.1879$ (all data)							
largest diffraction peak and hole / e·Å <sup>-3</sup>	1.872 and –2.181	1.570 and –1.432	1.076 and –0.765	1.867 and –1.693							

С

(PPh₄)₂[Re<sup>V</sup>(CN)₄(N)(MeOH)]·3MeOH (**Re-MeOH**)

(b)

PPh<sub>4</sub>

 $(PPh_4)_2[Re^{V}(CN)_4(N)(3pcn)] \cdot 0.45CH_2Cl_2(Re-pcn)$ 

Re1/2



**Fig. S11** The comparison of the crystal structures of **Re–MeOH** (a),<sup>58</sup> **Re–3pcn** (b), **Re–3pca** (c), **Re–3paa** (d), **Re–dppy** (e), and **Cu–dppy** (f)<sup>S10</sup> reference compounds, including the structural views presented along the selected crystallographic axis and the enlarged view of Cu<sup>1</sup> or Re<sup>V</sup> complexes present in the crystal structure. Related detailed structural parameters are gathered in Table S8. Note that compound **Re–3paa** presented in the (d) part reveals a significant structural disorder represented by two crystallographic positions of the Re1 complex with partial occupancies. Only a single set of two alternative sets of the positions of the related atoms is here visualized.

compound		Re-MeOH	e–MeOH <sup>sa</sup> Re–3pcn <sup>a</sup>			F	Re-3pca		Re-3paa	
complex				tr	rans-[Re1 <sup>v</sup> (	(CN)4(N)	(L)] <sup>2-</sup>			
L		MeOH		3pcn			Зрса		Зрра	
Re1–C/ Å		2.098(6)-2.1	15(7)	2.092(8)-	-2.124(8)	2.092	(9)–2.118(10)	-	1.89(4)-2.44(4)	
Re1≡N1 / Å		1.652(6)		1.679(6)/	/1.666(6)	:	1.647(8)	1	1.53(5)–1.95(6)	
Re1–L/Å		2.439		2.517(6)/ 2.517(5)			2.494(7)		2.516(16)- 2.541(15)	
C–Re1–C ( <i>cis</i> ) /	0	87.7(2)-90.0(2)		84.5(3)-	-91.3(3)	84.4	(3)-92.5(3)	6	4.9(15)-99.0(2)	
C–Re1–C (trans)	/ °	160.8(3)-164.4(3)		158.6(3)-164.0(3)		161.9(3), 163.4(3)			152.9(16)- 167.4(17)	
C–Re1≡N1/°		97.7(3)-99.7(3)		97.0(3)-102.2(3)		97.6	97.6(4)-99.8(3)		81.2(2)-121.2(19)	
C-Re1-L/°		79.2(3)-82.	5(3)	79.0(2)-84.6(2)		80.1	.(3)-83.0(3)	79	9.9(10)-96.8(15)	
N1≡Re1–L/°		178.7(3)		177.2(2)/176.3(2)			177.2(3)		170.2(14)- 172.5(13)	
compound					Re-dp	ру				
complex				mer	–[Re1 <sup>v</sup> (CN)	₃(N)(dp	ру)]⁻			
Re1–C / Å		2.069(13) -2.086(12)	C– (tro	Re1–C ans) / °	160.5	(4)	N1≡Re1–N5,	/ 0	165.2(3)	
Re1≡N1/Å		1.654(8)	C−R€	e1≡N1/°	99.8(4 106.3	1)— (4)	N1≡Re1-P1/	/ 0	102.1(3)	
Re1–N5 / Å		2.477(7)	C–Re	1–P1 ( <i>cis</i> ) / °	89.7(3), 8	9.9(3)	N5-Re1-P1/	/ 0	63.08(18)	
Re1–P1 / Å		2.412(2)	C—I (tre	Re1—P1 ans) / °	151.7	(3)	-		_	
C–Re1–C ( <i>cis</i> ) /°	85	.3(4), 85.8(4)	C–Re	e1=N5 / °	80.7(3)-8	8.6(3) -			_	

Table S8 Detailed structural parameters of Re<sup>V</sup> complexes in Re–MeOH,<sup>S6</sup> Re–3pcn, Re–3pca, Re–3paa, and Re–dppy reference compounds.



**Fig. S12** (part 1/2) Detailed characteristics of solid-state photoluminescent properties of **Re–MeOH** (a, b),<sup>58</sup> **Re–3pcn** (c, d), **Re–3pca** (e, f), **Re–3paa** (g, h), **Re–dppy** (i, j), **Cu–dppy** (k, I)<sup>S10</sup> reference compounds, as well as the dppy ligand (m, n), including excitation and emission spectra (a, c, e, g, I, k, and m) well as emission decay profiles (b, d, f, h, j, I, and n) under the indicated excitation and emission wavelengths at 300 K (solid lines) and 77 K (dashed lines), together with respective emission colors presented on the CIE 1931 chromaticity diagram (o). For the emission decay profiles, the mono-exponential fitting was applied, and the related best-fit curves are illustrated by solid lines in the (b), (d), (f), (h), (j), (I), and (n) parts. The related spectroscopic and CIE 1931 chromaticity parameters, as well as the best-fit parameters for the emission decay profiles fitting, are gathered in Table S9.



**Fig. S12** (part 2/2) Detailed characteristics of solid-state photoluminescent properties of **Re–MeOH** (a, b),<sup>S8</sup> **Re–3pcn** (c, d), **Re–3pca** (e, f), **Re–3paa** (g, h), **Re–dppy** (i, j), **Cu–dppy** (k, I)<sup>S10</sup> reference compounds, as well as the dppy ligand (m, n), including excitation and emission spectra (a, c, e, g, I, k, and m) well as emission decay profiles (b, d, f, h, j, I, and n) under the indicated excitation and emission wavelengths at 300 K (solid lines) and 77 K (dashed lines), together with respective emission colors presented on the CIE 1931 chromaticity diagram (o). For the emission decay profiles, the mono-exponential fitting was applied, and the related best-fit curves are illustrated by solid lines in the (b), (d), (f), (h), (j), (I), and (n) parts. The related spectroscopic and CIE 1931 chromaticity parameters, as well as the best-fit parameters for the emission decay profiles fitting, are gathered in Table S9.

**Table S9** Selected spectroscopic parameters of the solid-state photoluminescent properties of **Re–MeOH**,<sup>S6</sup> **Re–3pcn**, **Re–3pca**, **Re–3paa**, **Re–dppy**, **Cu–dppy**<sup>S8</sup> reference compounds, as well as the dppy ligand, for indicated excitation wavelengths ( $\lambda_{exc}$ ) at 300 and 77 K, including emission pattern maxima ( $\lambda_{em}^{max}$ ), the CIE 1931 chromaticity x and y parameters, absolute quantum yield ( $\Phi_{em}$ , room-temperature value only), bestfit parameters for the emission decay profiles to the mono-exponential decay function, as well as radiative ( $k_r$ ) and nonradiative ( $k_{nr}$ ) decay rate constant for the relaxation of the emissive state.

т/к	λ <sub>exc</sub> / nm	λ <sub>em</sub> <sup>max</sup> / nm	CIE : chrom paran	CIE 1931emission lifetimechromaticity		931 aticity emission lifetime eters $ olimits p_{em}$		decay cons / 10	∕rate tant <sup>a</sup> ⁴s <sup>-1</sup>				
	,		x	у		τ / μs	$\chi^2$	k <sub>r</sub>	k <sub>nr</sub>				
Re-MeOH <sup>S6</sup>													
300	430	527	0.358	0.583	0.13	1.2	-	10.83	72.50				
77	430	496, <u>523</u> , 552	0.359	0.583	-	77	-	-	-				
Re–3pcn													
300	430	565	0.467	0.523	0.78	24.5( <u>+</u> 0.08)	1.091	3.18	0.90				
77	430	565	0.450	0.5353	-	95.1( <u>+</u> 0.94)	1.087	-	-				
Re-3pca													
300	430	550	0.426	0.555	0.82	39.8( <u>+</u> 0.13)	1.116	2.06	0.45				
77	430	525, <u>550</u> , 580, 615	0.401	0.566	_	170.3(±2.21)	1.018	_	_				
				F	Re-3paa								
300	430	595	0.535	0.461	0.88	28.2( <u>±</u> 0.24)	1.059	3.12	0.43				
77	430	<u>595</u> , 612	0.532	0.464	I	157.1( <u>+</u> 5.86)	1.037	_	-				
				F	le-dppy								
300	430	600	0.552	0.446	0.05	15.0( <u>±</u> 0.22)	1.003	0.33	6.33				
77	430	600, <u>625</u>	0.564	0.434	-	20.9( <u>±</u> 0.05)	1.098	-	-				
				C	u– <b>dppy</b> <sup>s8</sup>								
300	305	560	0.428	0.516	0.92	26.1(±1.11)	1.097	3.52	0.31				
77	305	460	0.163	0.164	_	421.5(±2.79)	1.072	_	_				
				dp	py ligand								
300	_	_	-	-	_	-	_	-	-				
77	315	485	0.205	0.312	_	$1.7 \cdot 10^{-3}$ (±0.12)	1.112	_	-				

<sup>a</sup>Radiative ( $k_r$ ) and nonradiative ( $k_{nr}$ ) decay rate constant for the relaxation of the emissive state are based on the relationship  $k_r = \Phi_{em}/\tau$  and  $\Phi_{em} = k_r/(k_r+k_{nr})$  in which  $\tau$  values are the luminescence lifetime and the  $\Phi_{em}$  is the quantum yield.<sup>S9</sup>

Table	S10	The	set	of	selected	spectroscopic	data	of	the	other	reported	compounds	based	on
tetracyanidonitridorhenate(V) complexes. <sup>[S5,S6,S8,S9,S18]</sup>														

compound <sup>a</sup>	energy diff. <sup>c</sup> / cm <sup>-1</sup>	$\pmb{\varPhi}_{em}$	decay rate constant / 10 <sup>4</sup> s <sup>-1</sup>		emissive state	ref.
			<i>k</i> r	<i>k</i> nr		
(PPh₄)₂[Re <sup>v</sup> (CN)4(N)(MeOH)]	4	0.13	11.30	75.65	<sup>3</sup> [(d <sub>xy</sub> ) <sup>1</sup> (d <sub>π*</sub> ) <sup>1</sup> ] ( <sup>3</sup> MC)	[S8]
(PPh <sub>4</sub> ) <sub>2</sub> [Re <sup>v</sup> (CN)4(N)(acetone)]	2	0.34	1.62	3.14	<sup>3</sup> [(d <sub>xy</sub> ) <sup>1</sup> (d <sub>π*</sub> ) <sup>1</sup> ] ( <sup>3</sup> MC)	[S8]
(PPh <sub>4</sub> ) <sub>2</sub> [Re <sup>v</sup> (CN)4(N)(py)]	1	0.93	2.1	0.16	<sup>3</sup> [(d <sub>xy</sub> ) <sup>1</sup> (d <sub>π*</sub> ) <sup>1</sup> ] ( <sup>3</sup> MC)	[S9]
(Medabco) <sub>2</sub> [Re <sup>v</sup> (CN)4(N)(dae)]	9	0.28	0.792	2.08	<sup>3</sup> [(d <sub>xy</sub> ) <sup>1</sup> (d <sub>π*</sub> ) <sup>1</sup> ] ( <sup>3</sup> MC)	[\$5]
(Medabco) <sub>2</sub> [Re <sup>v</sup> (CN)4(N)(dap)]	16	0.22	0.649	2.3	<sup>3</sup> [(d <sub>xy</sub> ) <sup>1</sup> (d <sub>π*</sub> ) <sup>1</sup> ] ( <sup>3</sup> MC)	[\$5]
(PPh <sub>4</sub> ) <sub>2</sub> [Re <sup>v</sup> (CN)4(N)(3bzpy)]	9	0.36	2.7	4.8	<sup>3</sup> MLCT	[\$9]
(PPh <sub>4</sub> ) <sub>2</sub> [Re <sup>v</sup> (CN)4(N)(bpy)]	6	0.18	2.7	12	<sup>3</sup> MLCT	[\$9]
(PPh <sub>4</sub> ) <sub>2</sub> [Re <sup>V</sup> (CN)4(N)(pz)]	26	0.05	4	81	<sup>3</sup> MLCT	[S9]
(PPh <sub>4</sub> ) <sub>2</sub> [Re <sup>v</sup> (CN)4(N)(cpy)]	33	0.01	4	400	<sup>3</sup> MLCT	[S9]
(PPh <sub>4</sub> ) <sub>2</sub> [Re <sup>v</sup> (CN)4(N)(4bzpy)]	57	0.01	-	2600	<sup>3</sup> MLCT	[\$9]
$(PPh_4)_4 \{ [Re^{\vee}(CN)4(N)]_2(dae) \}$	1	0.67	3.4	1.7	<sup>3</sup> [(d <sub>xy</sub> ) <sup>1</sup> (d <sub>π*</sub> ) <sup>1</sup> ] ( <sup>3</sup> MC)	[S18]
(PPh <sub>4</sub> ) <sub>4</sub> {[Re <sup>v</sup> (CN)4(N)] <sub>2</sub> (bpy)}	32	0.31	3.4	7.5	<sup>3</sup> MLCT	[S18]
(PPh <sub>4</sub> ) <sub>4</sub> {[Re <sup>v</sup> (CN)4(N)] <sub>2</sub> (bpac)}	75	0.37	5.9	10.1	<sup>3</sup> MLCT	[S18]
(PPh <sub>4</sub> ) <sub>4</sub> {[Re <sup>v</sup> (CN)4(N)] <sub>2</sub> (bpee)}	22	0.01	-	-	<sup>3</sup> MLCT	[S18]
(PPh <sub>4</sub> ) <sub>4</sub> {[Re <sup>v</sup> (CN)4(N)] <sub>2</sub> (bpen)}	1	0.64	1.5	0.8	mixed ( <sup>3</sup> MLCT/ <sup>3</sup> MC)	[S18]
(PPh <sub>4</sub> ) <sub>4</sub> {[Re <sup>v</sup> (CN)4(N)] <sub>2</sub> (bpbp)}	9	0.71	3.0	1.0	mixed ( <sup>3</sup> MLCT/ <sup>3</sup> MC)	[S18]
{[Sr <sup>II</sup> (bpy) <sub>0.5</sub> (MeOH) <sub>2</sub> ]- [Re <sup>v</sup> (CN) <sub>4</sub> (N)(bpy) <sub>0.5</sub> ]} <sub>n</sub>	5	0.04	0.53	12.66	<sup>3</sup> MLCT	[S6]
1 <sup>b</sup>	55	0.56	4.59	3.61	mixed ( <sup>3</sup> MLCT/ <sup>3</sup> MC)	this work
2 <sup>b</sup>	5	0.72	3.98	1.55	mixed ( <sup>3</sup> MLCT/ <sup>3</sup> MC)	this work
3 <sup>b</sup>	5	0.75	2.31	0.77	mixed ( <sup>3</sup> MLCT/ <sup>3</sup> MC)	this work
4 <sup>b</sup>	0	0.84	3.10	0.59	mixed ( <sup>3</sup> MLCT/ <sup>3</sup> MC)	this work

<sup>a</sup> py, pyridine; Medabco, 1-methyl-1,4-diazabicyclo-[2.2.2]octan-1-ium; dae, 1,2-diaminoethane; dap, 1,3diaminopropane; 3bzpy, 3-benzoylpyridine; bpy, 4,4'-bipyridine; pz, pyrazine; cpy, 4-cyanopyridine; 4bzpy, 4-benzoylpyridine; bpac, 1,2-bis(4-pyridyl)acetylene; bpee = 1,2-bis(4-pyridyl)ethylene; bpen = 1,2-bis(4pyridyl)ethane; bpbp, 4,4'-bis(4-pyridyl)biphenyl. <sup>b</sup>The spectroscopic parameters for the PL properties only for the representative 430 nm excitation. <sup>c</sup>The energy difference between the emission maximum wavelength at 300 and 77 K.



**Fig. S13** (part 1/2) Detailed characteristics of solid-state photoluminescent properties of the air-dried powder sample of **1'** (a-d), **2'** (e-h), **3'** (i-l), **4'** (m-p), including excitation and emission spectra (a, c, e, g, i, k, m, and o) as well as emission decay profiles (b, d, f, h, j, l, n, and p) under the indicated excitation and emission wavelengths at 300 K and 77 K. For the emission decay profiles, the mono-exponential fitting was applied, and the related best-fit curves are illustrated by solid lines in the (b), (d), (f), (h), (j), (l), (n), and (p) parts. The related spectroscopic parameters, as well as the best-fit parameters for the emission decay profiles fitting, are gathered in Table S11.



**Fig. S13** (part 2/2) Detailed characteristics of solid-state photoluminescent properties of the air-dried powder sample of **1'** (a-d), **2'** (e-h), **3'** (i-l), **4'** (m-p), including excitation and emission spectra (a, c, e, g, i, k, m, and o) as well as emission decay profiles (b, d, f, h, j, l, n, and p) under the indicated excitation and emission wavelengths at 300 K and 77 K. For the emission decay profiles, the mono-exponential fitting was applied, and the related best-fit curves are illustrated by solid lines in the (b), (d), (f), (h), (j), (l), (n), and (p) parts. The related spectroscopic parameters, as well as the best-fit parameters for the emission decay profiles fitting, are gathered in Table S11.

**Table S11** Selected spectroscopic parameters of the solid-state photoluminescent properties of the airdried powder samples of **1'**, **2'**, **3'**, and **4'** for indicated excitation wavelengths ( $\lambda_{exc}$ ) at 300 and 77 K, including emission pattern maxima ( $\lambda_{em}^{max}$ ), the CIE 1931 chromaticity x and y parameters, absolute quantum yield ( $\Phi_{em}$ , RT value only), best-fit parameters for the emission decay profiles to the monoexponential decay function, as well as radiative ( $k_r$ ) and nonradiative ( $k_{nr}$ ) decay rate constant for the relaxation of the emissive state.

comp.	<i>т  </i> к	λ <sub>exc</sub> / nm	λ <sub>em</sub> <sup>max</sup> / nm	$\pmb{\varPhi}_{em}$	CIE 1931 chromaticity parameters		emission lifetime		decay rate constant <sup>a</sup> / 10 <sup>4</sup> s <sup>-1</sup>	
					x	У	τ / μs	$\chi^2$	<i>k</i> r	<i>k</i> <sub>nr</sub>
1'	300 <sup>b</sup>	430	600	0.63	0.523	0.461	17.2 ( <u>+</u> 0.89)	1.034	3.66	2.15
	77	430	570	-	0.512	0.483	96.1 (±2.11)	1.017	-	-
		290	480	-	0.283	0.349	232.1 ( <u>+</u> 2.77)	1.008	-	-
2'	300 <sup>b</sup>	430	610	0.75	0.550	0.434	23.7 ( <u>±</u> 0.98)	1.071	3.16	1.05
	77	430	592	_	0.527	0.460	122.9 ( <u>+</u> 1.45)	1.003	-	-
		290	480	-	0.263	0.339	227.4 ( <u>+</u> 1.82)	1.002	-	-
	300 <sup>b</sup>	430	604	0.79	0.562	0.432	39.0 ( <u>±</u> 0.56)	1.101	2.03	0.54
3'	77	430	603	-	0.569	0.423	169.5 ( <u>+</u> 1.16)	1.008	-	-
		290	510	-	0.321	0.409	234.7 ( <u>+</u> 3.06)	1.011	-	-
4'	300 <sup>b</sup>	430	601	0.87	0.548	0.445	32.3 (±1.11)	1.011	2.69	0.40
	77	430	602	-	0.571	0.427	157.4 ( <u>+</u> 1.66)	1.022	-	-
		290	496	-	0.317	0.378	222.1 ( <u>+</u> 4.17)	1.034	-	-

<sup>a</sup>Radiative ( $k_r$ ) and nonradiative ( $k_{nr}$ ) decay rate constant for the relaxation of the emissive state are based on the relationship  $k_r = \Phi_{em}/\tau$  and  $\Phi_{em} = k_r/(k_r+k_{nr})$  in which  $\tau$  values are the luminescence lifetime and the  $\Phi_{em}$  is the quantum yield.<sup>S9</sup> <sup>b</sup>The spectroscopic parameters for the PL properties at 300 K were presented only for the representative 430 nm excitation. The almost identical parameters for this temperature are observed for other excitation wavelengths, including the 290 nm excitation (for which the related parameters change distinctly upon cooling, see Fig. S13).

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