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Eu³⁺ Ternary and Tetrakis Complexes with Carbazole and Methyl Group Substituted Dibenzoylmethane Derivatives: Induction of Aggregation Enhanced Emission

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9 10 Abstract

Two dibenzoylmethane (DBM) derivatives with methyl (Me-DBM) or carbazole 11 (CBZ-DBM) substituents at the *para*-position of the phenyl ring and their four novel 12 ternary and tetrakis Eu³⁺ complexes with 1,10-phenanthroline (PHEN) as a secondary 13 ligand or tetraethylamonium ion $(N^+(Et)_4)$ as the counter-cation were synthesized and 14 characterized. The investigation of the optical properties of the complexes revealed 15 16 that Me-DBM based compounds exhibit aggregation enhanced emission (AEE), while in the case of CBZ-DBM this effect is not observed. At the same time, the 17 introduction of a carbazole substituent reduces the emission quantum yield of the 18 complexes. The decrease in luminescence efficiency for CBZ-DBM based Eu³⁺ 19 complexes is mainly attributed to the closely situated S₁ and T₁ energy levels of the 20 ligand that obstruct the intersystem crossing process. 21

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Keywords: Europium ternary complex, Europium tetrakis complex, partial energy
transfer process, aggregation enhanced emission, carbazole.

26 1. INTRODUCTION

Over the previous years the research interest in Eu^{3+} complexed β -diketones is 27 28 not decreasing due to a wide variety of potential application directions found in amplifiers for optical communication [1], as luminescent probes in biological samples 29 30 [2], in solar cells [3], as well as in the emissive layers of organic light emitting diodes (OLEDs) [4]. Also Eu^{3+} complexes have been used to fabricate red or white light 31 emitting diodes (LEDs) [5, 6]. The utilization of Eu^{3+} organic complexes in OLEDs 32 and LEDs can be specifically outlined, because of their distinctive emission properties 33 such as high emission efficiencies and sharp emission bands in the red-light region, 34 which provide high color purity for the devices. Additionally, Eu^{3+} complexes with β -35 diketone ligands usually have relatively simple and inexpensive steps of synthesis and 36 purification. 37

In order to obtain a brightly luminescent Eu³⁺ complex one must pay attention 38 to the design of organic ligands, so that their electronic configuration is compatible to 39 that of Eu³⁺ ion. To observe a full energy transfer process between the attached 40 ligands and the central metal ion, it is necessary that the triplet energy level of the 41 ligand is higher than the resonance level of the Eu^{3+} ion (17 250 cm⁻¹) [7]. Usually it 42 means that absorption bands of ligands should lie in near-UV region, however there 43 are some reports on the Eu^{3+} organic complexes with blue light absorbing ligands [8, 44 9]. Furthermore, for the purpose of practical applications it is also necessary, that the 45 Eu³⁺ complex exhibits a good solubility in commonly used solvents, so that the 46 fabrication process of the thin films containing these compounds would be simpler 47 and less costly. Finally, Eu³⁺ organic complexes should exhibit high thermal and 48 49 chemical stability.

In the recent years many authors have designed ligands, which contain organic
substituents that provide good solubility, charge transporting properties and high

thermal stability of the corresponding Eu³⁺ complexes. Carbazole, being an 52 inexpensive starting material and showing the previously discussed properties, is one 53 of the most commonly used amongst such chemical building blocks. Many 54 complexes, where carbazole is introduced to phenyltrifluorobutane-1,3-dione [10], 55 biphenyltrifluorobutane-1,3-dione [11] and phenylpropane-1,3-dione [12] para-56 position through a nitrogen atom have been synthesized. Alternatively, Eu³⁺ 57 complexes containing ligands, where carbazole is attached to β -diketone through 2-58 [8, 9, 13] and 3- [14-16] position of carbazole ring, are reported. Some authors have 59 chosen to attach the carbazole group in secondary ligands, for example in 1,10-60 phenanthroline unit [17, 18]. Independently from the position of the attachment, Eu^{3+} 61 62 complexes with carbazole-functionalized β -diketone ligands usually exhibit bright red emission and they have potential application possibilities in biological imaging [14] 63 and in fabrication of white organic light emitting diodes (WOLED) [11] and red-light 64 OLEDs [10]. 65

Dibenzoylmethane (DBM), without the doubt, is one of the most used β -66 diketone type chelating ligands for the Eu³⁺ organic complexes. However, the 67 understanding of the consequences of carbazole group attachment to para-position of 68 this molecule through N-atom (CBZ-DBM) and its effects on the corresponding Eu^{3+} 69 complexes is poor. Only one report characterizing Eu^{3+} tris complex with this ligand 70 can be found [19]. It is known that *ternary* and *tetrakis* Eu^{3+} complexes usually 71 72 exhibit higher photoluminescence quantum yields (PLQY), longer lifetimes [7] as well as higher thermal stability and solubility. This improvement is attributed to the 73 replacement of the chelating solvent molecules in the complex by a secondary or the 74 fourth β -diketone ligand. Furthermore, only two *tetrakis* Eu³⁺ complexes with β -75 diketone ligands that contain carbazole group have been reported to date [10, 11], but 76

77 the mentioned compounds also contain a trifluorated methyl group in DBM fragment. study consists of the synthesis of two DBM derivatives - 4-78 This methyldibenzoylmethane (Me-DBM) and 4-carbazol-9-yl-dibenzoylmethane (CBZ-79 **DBM**) and the corresponding four novel Eu^{3+} complexes **C1-C4** (Scheme 1), with an 80 initial aim to assess the effects of the carbazole introduction. Structural 81 82 characterization as well as investigation of optical properties in different media and evaluation for OLED application use is reported. Ground state and excited state 83 energy level calculations are presented and discussed for ligands in order to explain 84 85 the experimental observations. The acquired results show that the emissive properties of the compounds can be drastically changed depending on the structure of the used 86 87 dibenzoylmethane derivative.



89Scheme 1. Synthesis of ligands Me-DBM, CBZ-DBM and complexes C1-C4; (a) – 1) NaH, THF, 6590°C; 2) H_2O , 10% HCl; (b) – 10% NaOH/ H_2O , 1,10-phenanthroline, EuCl₃·6H₂O; (c) – 10%91NaOH/ H_2O , N(Et)₄Br, EuCl₃·6H₂O; (d) Carbazole, Cu, 18-Crown-6, K₂CO₃, DMF, 155 °C.

92

93 2. EXPERIMENTAL SECTION

94 2.1. Materials and instrumentation

EuCl₃·6H₂O (99.99%) was purchased from *Acros Organics*, 1,10phenanthroline (99%), tetraethylammonium bromide (98%), 4-methylacetophenone
(96%), 4-iodoacetophenone from *Alfa Aesar*, methylbenzoate (99%) and carbazole
(≥95%) from *Sigma Aldrich*, but poly(*N*-vinylcarbazole) (PVK) from *ABCR*(GmbH&Co). All substances were used without further purification.

¹H NMR and ¹³C NMR spectra were recorded on a Brucker Avance 300 MHz 100 spectrometer in CDCl₃, DMSO-D₆ or CD₃CN solutions. Chemical shifts were 101 expressed in parts per million (ppm) relative to solvent signal. CHN elemental 102 analysis was carried on Euro Vector EA 3000 analyzer. Infrared spectra were 103 104 recorded on a Perkin-Elmer Spectrum 100 FTIR spectrometer using KBr pellets (4000 to 650 cm⁻¹). The thermogravimetric analysis was performed on a Perkin Elmer STA 105 6000 instrument. Each sample was heated from 30-900 °C with heating rate 10 106 °C/min in the nitrogen atmosphere. Low resolution mass spectra of ligands were 107 acquired on a Waters EMD 1000MS mass detector (ESI+ mode, voltage 30 V). The 108 UV/Vis absorption spectra were acquired with Perkin-Elmer 35 UV/Vis spectrometer 109 using 1 cm length quartz cuvettes. Emission and excitation spectra were measured on 110 QuantaMaster 40 steady state spectrofluorometer (Photon Technology International, 111 112 Inc.). For triplet level measurements low-temperature phosphorescence spectra were acquired at 77 K in 2-methyltetrahydrofuran solution on the same device. The singlet 113 and triplet energy levels were determined at the emission band maxima. The lifetime 114 measurements were carried out in room temperature using the 115 same spectrofluorometer equipped with high power Xenon flash lamp as excitation source. 116 Lifetime data were processed by OriginPro 8 program. Absolute photoluminescence 117 quantum yields (PLQY) were determined using the same spectrofluorometer equipped 118

119 with 6 inch integrating sphere by LabSphere and special holders for cuvette, film and powder samples. The PLQY were calculated by software supplied by Photon 120 Technology International, Inc. Polymer films were obtained with Laurell WS-400B-121 122 NPP/LITE spin coater (Parameters: speed 800 rpm, acceleration 800 rpm/s for 1 min). Density functional theory (DFT) has been performed using ORCA program version 123 4.0.1 [20]. The geometry optimization of ligands was obtained using non-local 124 functional B3LYP with 6-311G^{**} [21] basis set. For singlet and triplet energy level 125 calculations def2-TZVP basis [22] and def2/J [23] auxiliary basis were used. 126

127

128 **2.2. Synthesis**

129 The synthesis of dibenzoylmethane derivatives as well as complexes C1-C4 is130 shown in Scheme 1.

131 2.2.1. Synthesis of compounds DBM derivatives

(Z)-3-hydroxy-3-phenyl-1-(p-tolyl)-prop-2-en-1-one Me-DBM . To a methyl benzoate 132 (1) (1.15 g, 8.45 mmol), placed in two-neck round-bottom flask, dry THF (15 mL) 133 and NaH 60% dispersion in mineral oil (0.34 g, 8.45 mmol) was added. Reaction 134 mixture was refluxed until all H₂ is released from solution. Afterwards, 4-135 methylacetophenone (2) (1.03 g, 7.68 mmol) dissolved in dry THF (5 mL) was added 136 dropwise with dropping funnel and resulting mixture was refluxed for four hours. 137 Then reaction mixture was cooled with ice bath to room temperature and neutralized 138 with 10% HCl solution until pH ~7. Water (10 mL) and CHCl₃ (40 mL) was added 139 and organic fraction was separated, washed with water (2 x 50 mL) and dried with 140 anhydrous Na₂SO₄. The Solution was filtered and filtrate was evaporated. Obtained 141 precipitate was crystalized from *i*-PrOH (30 mL) and 1.01 g of compound Me-DBM 142 was obtained as yellow powder. Yield 55%; m.p.= 80-81 °C. ¹H NMR (300 MHz, 143 DMSO-D₆, ppm): δ= 8.17 (2H, d, J=6.0 Hz, H-Ph); 8.12 (2H, d, J=6.0 Hz, H-Ph); 144

145 7.69-7.62 (1H, m, H-Ph); 7.58 (2H, d, J=9.0 Hz, H-Ph); 7.38 (2H, d, J=9.0 Hz, H-Ph); 7.32 (1H, s, -C<u>H</u>=C(OH)-); 2.41 (3H, s, -CH₃). ¹³C NMR (75 MHz, DMSO-D₆, ppm): 146 δ = 186.1; 185.1; 144.0; 135.0; 133.4; 132.4; 129.9; 129.3; 128.0; 127.8; 93.4; 21.6. 147 cm^{-1}): 3129, 3066, FT-IR. (KBr. 3038. 2924, 2855. 1599. 1520. 148 MS, $C_{16}H_{14}O_2$ requires $[M+H]^+$ 239.10; found $[M+H]^+$ 239.2. Anal. Calcd. For 149 C₁₆H₁₄O₂: C, 80.65; H, 5.92; found C, 80.44; H, 5.67. 150

151 (Z)-3-hydroxy-3-(4-iodophenyl)-1-phenylprop-2-en-1-one (4). Two-neck roundbottom flask containing dry THF (15 mL) and NaH 60% dispersion in mineral oil 152 (1.60 g, 40.00 mmol) was purged with Argon and cooled to 0 °C with ice bath. Then 153 methyl benzoate (1) (3.00 g, 22.00 mmol) was added. After 10 minutes 4-154 155 iodoacetophenone (3) (5.00 g, 20.00 mmol) dissolved in dry THF (5 mL) was added dropwise with dropping funnel and resulting mixture was refluxed for six hours. 156 Afterwards, ethylacetate (15 mL) and water (10 mL) was added and reaction mixture 157 was neutralized with 10% HCl solution until pH ~7. Organic fraction was separated, 158 washed with water (2 x 50 mL) and brine (2 x 25 mL), and dried with anhydrous 159 Na₂SO₄ Solution was filtered and filtrate was evaporated. Obtained precipitate was 160 crystalized from CH₂Cl₂: ethylacetate (2:1) system and 3.24 g of compound 4 was 161 obtained as light brown powder. Yield 46%; m.p.= 105-107 °C. ¹H NMR (300 MHz, 162 CDCl₃, ppm): δ= 7.99 (2H, d, J=6.0 Hz, H-Ph), 7.85 (2H, d, J=9.0 Hz, H-Ph), 7.71 163 (2H, d, J=9.0 Hz, H-Ph), 7.61-7.48 (3H, m, H-Ph), 6.83 (1H, s, -CH=C(OH)-). ¹³C 164 NMR (75 MHz, CDCl₃, ppm): δ= 186.1; 184.7; 138.0; 135.3; 135.0; 132.7; 128.8; 165 128.6; 127.2; 99.9; 93.0. FT-IR, (KBr, cm⁻¹): 3436, 3059, 2955, 2926, 1584, 1564, 166 1508. MS, C₁₅H₁₁IO₂ requires [M+H]⁺ 350.98; found [M+H]⁺ 351.1. Anal. Calcd. For 167 C₁₅H₁₁IO₂: C, 51.45; H, 3.17; found C, 51.22; H, 2.97. 168

169 (Z)-1-(4-(9H-carbazol-9-yl)phenyl)-3-hydroxy-3-phenylprop-2-en-1-one CBZ-DBM. 170 Two-neck round-bottom flask was purged with Argon and then diketone (4) (1.50 g, 4.29 mmol), carbazole (0.72 g, 4.29 mmol), K₂CO₃ (2.30 g, 16.80 mmol), activated 171 Cu (0.53 g, 8.58 mmol), 18-Crown-6 (0.38 g, 1.43 mmol) and dry DMF (7.5 mL) 172 were added. Reaction mixture was refluxed at 155 °C for four hours. Then it was 173 cooled to room temperature and water (10 mL) was added. Reaction mixture was 174 extracted with CH₂Cl₂ (3 x 25 mL) and organic fraction was separated, evaporated 175 and obtained precipitate was dissolved in CH₂Cl₂:MeOH (1:1) system. From this 176 solution green precipitate was obtained, filtered and then dried in room temperature. 177 Afterwards to green precipitate ethanol (30 mL) and 10% NaOH solution (5 mL) was 178 added and resulting mixture was refluxed for 20 minutes. The insoluble precipitate 179 was filtered off and filtrate was neutralized with 10% HCl solution. Yellow 180 precipitate (0.24 g) was formed, filtered and dried. Yield 14%; m.p.= 126-129 °C. ¹H 181 NMR (300 MHz, CDCl₃, ppm): δ= 8.27 (2H, d, J=9.0 Hz, H-Ph-CBZ), 8.19 (2H, d, 182 J=9.0 Hz, H-Ph), 8.07 (2H, d, J=6.0 Hz, H-Ph), 7.76 (2H, d, J=9.0 Hz, H-Ph-CBZ), 183 7.62-7.45 (7H, m, H-Ph-CBZ, H-Ph), 7.36 (2H, t, J=9.0 Hz, H-Ph-CBZ), 6.98 (1H, s, 184 -CH=C(OH)-). ¹³C NMR (75 MHz, CDCl₃, ppm): δ= 186.0; 184.7; 141.6; 140.3; 185 135.4; 134.1; 132.7; 129.0; 128.8; 127.3; 126.7; 126.2; 123.9; 120.6; 120.4; 109.8; 186 93.2. FT-IR, (KBr, cm⁻¹): 3436, 3055, 2926, 1602, 1516, 1224. MS, C₂₇H₁₉NO₂ 187 requires [M+H]⁺ 390.14; found [M+H]⁺ 390.3. Anal. Calcd. For C₂₇H₁₉NO₂: C, 83.27; 188 H, 4.92; N, 3.60; found C, 83.01; H, 4.71; N, 3.72. 189

190 2.2.2. Synthesis of complexes C1-C4

*Eu(Me-DBM)*₃*PHEN (C1)*. Solution of diketone Me-DBM (0.22 g, 0.92 mmol) in
ethanol (10 mL) was refluxed until complete dissolution. 1,10- Phenanthroline (0.06
g, 0.31 mmol) in ethanol (3 mL) was added, followed by addition of 10% NaOH

solution until pH~7-8. Afterwards, distilled water solution (5 mL) containing 194 EuCl₃·6H₂O (0.08 g, 0.31 mmol) was added dropwise and resulting solution was 195 stirred for 2 hours in the room temperature. Formed precipitate was separated by 196 suction filtration, washed with ethanol (10 mL) and distilled water (10 mL) and dried 197 in vacuum at 50 °C for 24 hours. Complex C1 was obtained as light yellow powder 198 (0.18 g). Yield 56%. ¹H NMR (300 MHz, CDCl₃, ppm): δ = 10.96 (2H, br s, H-199 PHEN), 10.58 (2H, br s, H-PHEN), 10.00 (2H, br s, H-PHEN), 8.97 (2H, br s, H-200 PHEN), 6.75 (9H, br s, H-Ph), 6.59 (6H, br s, H-Ph), 5.94 (12H, br s, H-Ph), 2.90 201 (3H, s, -CH=C(O)-), 2.40 (12H, s, -CH₃). FT-IR, (KBr, cm⁻¹): 3059, 3028, 2921, 202 1593, 1549, 1520, 1499, 1422. Anal. Calcd. For EuC₆₀H₄₇N₂O₆: C, 69.03; H, 4.54; N, 203 2.68; found C, 68.59; H, 4.32; N, 2.81. 204

 $[Eu(Me-DBM)_4]^{-}N^{+}(Et)_4$ (C2). Solution of diketone Me-DBM (0.25 g, 1.05 mmol) in 205 ethanol (10 mL) was refluxed until complete dissolution. Tetraethylammonium 206 bromide (0.06 g, 0.26 mmol) in ethanol (3 mL) was added, and then 10% NaOH 207 solution was added until pH~7-8. Afterwards, EuCl₃·6H₂O (0.07 g, 0.26 mmol) in 208 distilled water (5 mL) was added dropwise and resulting solution was stirred for 2 209 hours in the room temperature. Formed precipitate was filtrated, washed with ethanol 210 (10 mL), distilled water (10 mL) and dried in vacuum at 50 °C for 24 hours. 0.19 g of 211 light yellow powder (C2) was obtained. Yield 59%. ¹H NMR (300 MHz, CD₃CN, 212 ppm): δ=7.70 (8H, br s, H-Ph), 7.65 (8H, d, J=9.0 Hz, H-Ph), 7.25 (12H, br s, H-Ph), 213 7.08 (8H, d, J=9.0 Hz, H-Ph), 5.93 (4H, s, -CH=C(O)-), 3.23 (8H, q, (CH₃-CH₂)₄N⁺), 214 2.53 (12H, s, Ph-CH₃), 1.25 (12H, m, (CH₃-CH₂)₄N⁺). FT-IR, (KBr, cm⁻¹): 3056, 215 3029, 2985, 2921, 2859, 1596, 1552, 1519, 1498, 1423, 1307, 1289. Anal. Calcd. For 216 EuC₇₂H₇₂NO₈: C, 70.23; H, 5.89; N, 1.14; found C, 70.11; H, 5.75; N, 0.98. 217

218 $Eu(CBZ-DBM)_3PHEN$ (C3). Complex was synthesized by the same procedure as for C1, except diketone CBZ-DBM was used instead of compound Me-DBM. Light 219 brown powder. Yield 67%. ¹H NMR (300 MHz, CDCl₃, ppm): δ = 11.08 (2H, br d, H-220 PHEN), 10.67 (2H, br s, H-PHEN), 10.24 (2H, br s, H-PHEN), 9.08 (2H, br d, H-221 PHEN), 8.12-8.10 (6H, br d, H-Ph-CBZ), 7.34-7.21 (24H, m, H-Ph-CBZ, H-Ph), 222 6.95-6.90 (15H, m, H-Ph-CBZ, H-Ph), 6.44-6.08 (9H, m, H-Ph, -CH=C(O)-). FT-IR, 223 (KBr, cm⁻¹): 3051, 2959, 2926, 2852, 1598, 1547, 1500, 1423. Anal. Calcd. For 224 EuC₉₃H₆₂N₅O₆: C, 74.59; H, 4.17; N, 4.68; found C, 74.12; H, 4.32; N, 4.29. 225

226 $[Eu(CBZ-DBM)_4]^{*}N^{+}(Et)_4$ (C4). Complex was synthesized by the same procedure as for C2, except diketone CBZ-DBM was used instead of compound Me-DBM. Light 227 brown powder, Yield 30%. ¹H NMR (300 MHz, CDCl₃, ppm): $\delta = 8.27$ (8H, d, J=9.0 228 Hz, H-Ph-CBZ), 8.18 (8H, d, J=6.0 Hz, H-Ph-CBZ), 8.06 (8H, d, J=6.0 Hz, H-Ph-229 CBZ), 7.78 (8H, d, J=9.0 Hz, H-Ph-CBZ), 7.62-7.32 (36H, m, H-Ph), 6.97 (4H, s, -230 CH=C(O)-), 3.79-3.75 (8H, m, CH₃-CH₂)₄N⁺), 1.32-1.24 (12H, m, (CH₃-CH₂)₄N⁺). 231 FT-IR, (KBr, cm⁻¹): 3057, 2926, 1596, 1548, 1500, 1306, 1226. Anal. Calcd. For 232 EuC₁₁₆H₉₂N₅O₈: 75.89; H, 5.05; N, 3.81; found C, 75.44; H, 4.93; N, 4.08. 233

234 **2.3. OLED preparation**

Sandwich type samples with the pixel size of 16 mm^2 were prepared with the 235 ITO/PEDOT:PSS(40nm)/C1(50nm)/TPBi(20nm)/LiF(1nm)/ following structure 236 Al(100nm) for the host free device and ITO/PEDOT:PSS(40nm)/PVK:C1(50nm) 237 (10wt%)/TPBi(20nm)/LiF(1nm)/Al(100nm) for hosted device, where Poly(3,4-238 ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), 239 2,2',2"-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) and LiF were used as hole-240 injection, electron transport and electron-injection layers, respectively, and poly(N-241

242 vinylcarbazole) (PVK) as hole-transporting host for the emitter. Indium Tin Oxide (ITO) glass (Präzisions Glas & Optik GmbH) with a sheet resistivity of 15 Ω /square 243 was used as a substrate. A 12 mm wide ITO strip line was made by wet etching at the 244 245 middle of the substrate. ITO substrates were cleaned by the following method: sonicated in CHCl₃; sonicated in acetone; 2x rinsed with deionized (DI) water; 246 sonicated in water with 3 vol% of Hellmanex II detergent; rinsed with DI water; 247 sonicated in DI water and isopropyl alcohol. Before deposition of PEDOT:PSS the 248 ITO glass was blown dry with nitrogen and treated by UV-ozone for 20 min. ITO 249 layer was covered with PEDOT:PSS (from H.C. Starck, Al4083) using spin coater 250 Laurell WS650. Rotation lasted for 1 minute with speed 2000 rpm. The sample was 251 252 moved in a glovebox and heated at 200 °C for 10 minutes. The solution of emitting layer compounds with a concentration of 5 mg/mL was spin-coated on the 253 PEDOT:PSS layer with 2000 rpm for 40 sec and heated at 120 °C for 15 minutes 254 afterwards. Further the samples were moved from glovebox to vacuum chamber, 255 256 without the exposure to air, for thermal evaporation of electron transport TPBi (Sigma Aldrich 806781) electron-injection LiF (Sigma Aldrich 449903) and electrodes at the 257 pressure $6 \cdot 10^{-6}$ Torr. The deposition speed was 1Å/s, 0.1 Å/s and 5 Å/s for TPBi, LiF 258 and Al, respectively. In the end the samples were encapsulated using two component 259 epoxide. The current-voltage characteristics of the OLEDs were measured by the 260 multimeter Keithley 2700 and the voltage source was Keithley 230 unit. The 261 electroluminescence brightness was measured by Konica Minolta Luminance and 262 Color Meter CS-150. 263

264 **3. RESULTS AND DISCUSSION**

265 **3.1.** Synthesis and characterization of ligands and Eu³⁺ complexes

266 The synthetic route to the β -diketone ligands **Me-DBM** and **CBZ-DBM** and their Eu³⁺ ternary and tetrakis complexes is shown in Scheme 1. The ligand Me-DBM was 267 prepared by Claisen condensation reaction between methyl benzoate (1) and 4-methyl 268 acetophenone (2) with a moderate yield – 55%. The other β -diketone **CBZ-DBM** was 269 obtained by two-step synthesis. In the first stage 4-iododibenzoylmethane (4) was 270 obtained in the Claisen condensation reaction between methyl benzoate (1) and 4-271 iodoacetophenone (3). Afterwards, CBZ-DBM was prepared in Cu catalyzed Ullman 272 condensation reaction between 4-iododibenzoylmethane (5) and carbazole, with a 273 relatively low yield (14%). Eu^{3+} ternary complexes C1 and C3 were prepared by 274 mixing ligands PHEN, Me-DBM or CBZ-DBM and EuCl₃·6H₂O in the ratio 1:3:1 in 275 the presence of 10% NaOH. However, tetrakis complexes C2 and C4 were obtained 276 by taking tetraethylammonium bromide, Me-DBM or CBZ-DBM and EuCl₃·6H₂O in 277 the molar ratio 1:4:1 in the presence of 10% NaOH. The obtained ligands were 278 analyzed by FT-IR, ¹H NMR, ¹³C NMR spectroscopy and mass spectra data, but 279 newly synthesized Eu³⁺ complexes C1-C4 by FT-IR, ¹H NMR, elemental analysis 280 data and thermogravimetric analysis (TGA). Comparison of ¹H NMR spectra of the 281 ligand **CBZ-DBM** and its Eu^{3+} ternary complex **C3** are given in Fig. 1. As it can be 282 283 seen from Fig. 1 (a) free ligand CBZ-DBM in CDCl₃ solution exists in enol form and methine proton (H4) shows a signal at 6.98 ppm. Enolic proton (-OH) was not 284 observed, due to a rapid exchange of this proton with H₂O (traces in CDCl₃), which 285 usually render the signal too broad to be observed in ¹H NMR spectra. Protons from 286 carbazole cycle (H7-H10, H7'-H10') exhibit three well resolved signals at 8.27, 7.76 287 and 7.36 ppm with spin coupling constant of 9.0 Hz. However, signals of protons H8, 288 H8' overlap with protons from DBM fragment (H2, H2', H3, H6, H6') and form a 289 multiplet at 7.53 ppm. Remaining protons H1, H1' and H5, H5' show two well 290

resolved doublets at 8.19 and 8.07 ppm. ¹H NMR spectra of ligand CBZ-DBM show 291 changes upon complexation with Eu^{3+} ion (Fig.1 (b)). First of all, complexation with 292 Eu^{3+} ion leads to a proton signal broadening and shift to higher field. Four new broad 293 signals at 11.08, 10.67, 10.24 and 9.08 ppm appear in the ¹H NMR spectra and 294 correspond to the protons from 1,10-phenanthroline molecule (H11-H14, H11'-H14'). 295 Methine proton (H4) from **CBZ-DBM** molecule shows a shift to higher field at 6.19 296 ppm and overlaps with proton signals from phenyl group of DBM unit (H6 and H6'). 297 Furthermore, proton signals from the carbazole cycle (H7-H10, H7'-H10') are not 298 well resolved as it was for the free ligand and even overlaps with some proton signals 299 of DBM unit. Two signals – a broad doublet (8.11 ppm) and multiplets at 7.28 ppm 300 301 and 6.96 ppm were signed to protons H7-H10, H7'-H10'. Finally, remaining protons from DBM unit exhibit two broad multiplets at 7.28 and 6.96 ppm. In conclusion, ¹H 302 NMR spectra of complex C3 confirms that ligand ratio of PHEN to CBZ-DBM is 1:3 303 (8 protons:54 protons). Similar ¹H-NMR spectra and the same ligand ratio was 304 obtained for other newly synthesized *ternary* complex C1. 305

The ¹H NMR spectra of *tetrakis* complexes C2 and C4 contain two signals at 3.23 and 1.25 ppm (C2) (3.79 and 1.28 ppm for C4) in higher field region, which correspond to the protons of ethylene and methyl group in $N^+(Et)_4$ unit. Moreover, six signals of four **Me-DBM** ligands with an integral intensity of 52 protons or seven signals of four **CBZ-DBM** ligands with an integral intensity of 68 protons were observed at lower field and confirmed that these complexes contain one tetraethylammonium cation and four DBM ligands.



Fig. 1. (a) - ¹H NMR spectra of compound **CBZ-DBM** in CDCl₃ at 298 K; (b) – ¹H NMR spectra of Eu³⁺ *ternary* complex **C3** in CDCl₃ at 298 K.

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FT-IR spectra of free ligands Me-DBM and CBZ-DBM exhibit a broad band 317 around 3200-3600 cm⁻¹, which attributes to enolic –OH stretching vibrations. 318 319 Carbonyl group (C=O) stretching vibrations were found at 1599 (Me-DBM) and 1601 cm⁻¹ (**CBZ-DBM**). The observed strong absorption bands at region 1573-1500 cm⁻¹ 320 probably corresponds to enolic and aromatic C=C bond vibrations. However, for 321 complexes C1-C4 no broad band in the region above 3000 cm⁻¹ was observed, 322 indicating that DBM derivatives are coordinated to Eu³⁺ ion through diketone 323 324 fragment. For *tetrakis* complexes C2 and C4 sharp absorption bands in the region 3060-2850 cm⁻¹ are observed and attributes to aliphatic C-H vibrations of $N^+(Et)_4$ 325 unit. Furthermore, carbonyl group (C=O) stretching vibrations were found at lower 326 frequencies – at 1593 and 1594 cm^{-1} for complexes C1 and C2, and at 1597 and 1596 327 cm⁻¹ for C3 and C4. Similar changes between FT-IR spectra of the ligands and their 328 Eu³⁺ complexes were reported for other β -diketone complexes [24, 25]. Elemental 329 330 analysis data of complexes C1-C4 were in a good agreement with the proposed 331 structures.

332	Thermal stability of complexes C1-C4 was investigated by thermogravimetric
333	analysis (TGA) in inert atmosphere with a heating rate of 10 °C/min. Decomposition
334	temperatures of complexes C1 and C2 (275 and 234 °C) with Me-DBM ligands are
335	higher than the ones for complexes C3 and C4 with CBZ-DBM ligands (180 and 166
336	°C). It is apparent, that the introduction of carbazole moiety in DBM molecule
337	slightly decreases the thermal stability of Eu ³⁺ complexes, independently from a
338	complex structure. Although T_d for complexes C3 and C4 are below 200 °C, these
339	values are close to the reported decomposition temperatures (190-200 °C) for other
340	Eu^{3+} complexes with β -diketones that contain carbazole moiety [10, 11].

Ternary and *Tetrakis* complexes C1-C4 exhibit excellent solubility in
commonly used solvents, such as CH₂Cl₂, THF, CHCl₃, MeCN, EtOH.

343 **3.2.** Absorption properties of ligands and Eu³⁺ complexes

The UV/Vis absorption spectra of compounds PHEN, **Me-DBM**, **CBZ-DBM** and complexes **C1-C4** were measured in THF solutions ($c\sim1.5\cdot10^{-5}$ M) and are shown in Fig. 2.



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Fig.2. UV/Vis absorption spectra of compounds PHEN, **Me-DBM**, **CBZ-DBM** and their Eu³⁺ complexes **C1-C4** in THF solutions (c~1.5·10⁻⁵M).

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Secondary ligand PHEN shows a broad absorption band with maximum at 351 352 289 nm and high molar absorption coefficient ε (Table 1). β -Diketone Me-DBM exhibits a broad absorption band in near UV region (300-380 nm), centered at 347 353 nm, which attributes to the π - π ^{*} enolic transitions from β -diketone fragment. 354 Introduction of substituent (-Me) in DBM molecule leads to a small bathochromic 355 shift of the absorption spectra maxima by 5 nm, compared to the value reported for 356 DBM ($\lambda_{abs} = 343$ nm in THF) [26]. Ligand **CBZ-DBM** exhibits a wide absorption 357 band with maxima at 291 and 375 nm and two well separated low energy shoulders at 358 320 and 335 nm. These two low energy shoulders together with absorption at 291 nm 359 360 correspond to π - π * transitions of carbazole moiety [27], whereas λ_{abs} at 375 nm marks charge transfer (CT) transition due to a fact that carbazole moiety possesses electron 361 donating but carbonyl groups – accepting properties. To prove this statement DFT 362 calculation were carried for ligands Me-DBM and CBZ-DBM in order to obtain 363 optimized ground state structure geometries as well as HUMO and LUMO orbitals 364 (Fig. 3). HOMO orbital for Me-DBM are localized on 4-methylphenyl-β-diketone 365 unit, while LUMO resides on the whole molecule, illustrating a large HOMO-LUMO 366 overlap. However, for compound CBZ-DBM HOMO is localized on 1-(4-367 carbazolephenyl)-1,3-diketone unit and LUMO is contained on 3-phenyl-1,3-diketone 368 369 part, what indicates that, upon the excitation, a CT transition is expected for CBZ-DBM. 370



Fig. 3. HOMO and LUMO orbitals of optimized ground state structures of compounds **Me-DBM** and **CBZ-DBM**, obtained using B3LYP6-311G** set.

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373 374 375

The absorption spectra of Eu^{3+} complexes C1-C4 show a slightly different 376 behavior between Me-DBM and CBZ-DBM based compounds. While the band shape 377 in all cases almost completely mimics that of the free ligands, upon the complexation 378 the absorption peak of Me-DBM experiences a redshift. For CBZ-DBM based C4, on 379 the other hand, it remains almost unchanged, while for C3- slightly blueshifts. The 380 381 explanation of this difference between the two ligands can, once again, be explained by CT nature of **CBZ-DBM**, as upon the complexation the increased electron density 382 in diketonate fragment reduces the push-pull character of the molecule, increasing the 383 bandgap value. The complexation with Eu^{3+} ion is accompanied with an increase in 384 molar absorption coefficients for the lowest energy transitions: for *ternary* complexes 385 C1 and C3 ε is approximately three times higher, but for *tetrakis* complexes C2 and 386 $C4 \sim$ four times higher than the values measured for the free ligands, confirming yet 387 again, that in complexes C1, C3 Eu^{3+} is coordinated with three β -diketone ligands, but 388 in complexes C2 and C4 – with four β -diketone ligands. 389

390
391
392Table 1392
393UV/Vis absorption and luminescence spectral data of the ligands PHEN, Me-DBM, CBZ-DBM and
and
their complexes C1-C4 in THF (c~1.5 · 10⁻⁵M).
CompoundTable 1Table 1OUV/Vis absorption and luminescence spectral data of the ligands PHEN, Me-DBM, CBZ-DBM and
their complexes C1-C4 in THF (c~1.5 · 10⁻⁵M).Compound λ_{abs} , nm λ_{em} , nmPLQY I_2/I_1^a τ^b , μs

	$(\epsilon, 10^4 \mathrm{M}^{-1} \cdot \mathrm{cm}^{-1})$				
PHEN	289 (5.09)	-	-	-	-
Me-DBM	347 (2.45)	-	-	-	-
C1	356 (7.11)	611	0.03	29.8	143.60±0.24
C2	354 (9.45)	611	0.02	23.4	141.49±0.35
CBZ-DBM	291, 326, 341, 375 (2.11)	478	0.26	-	-
C3	292, 327, 342, 369 (6.34)	475, 611	0.10	12.1	38.88±0.22
C4	291, 326, 341, 374 (9.15)	476	0.26	-	-

394 ^a- intensity ratio between transitions ${}^{5}D_{0} \rightarrow {}^{7}F_{2}/{}^{5}D_{0} \rightarrow {}^{7}F_{1}$ from emission spectra.

395 ^b - luminescence lifetime.

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398 **3.3.** Photoluminescence studies of Eu³⁺ complexes in solution and solid state

Photoluminescence properties of the synthesized ligands and their Eu^{3+} 400 complexes were investigated in THF solutions (c~1.5·10⁻⁵M). Relevant data are 401 summarized in Table 1 and emission spectra are shown in Fig. 4 (a).

402 Ligand Me-DBM is completely non-emissive in THF solution. CBZ-DBM,

403 on the other hand, exhibits bright cyan-blue emission (Fig. 4. (b)) with maxima at 478
404 nm and moderate absolute photoluminescence quantum yield (PLQY) of 0.26.

405	Eu ³⁺ ternary and tetrakis complexes C1 and C2 with Me-DBM ligand show
406	only the narrow Eu^{3+} ion emission bands with multiple maximums at 580, 594, 611,
407	650 and 703 nm, corresponding to ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J=0-4) transitions. The emission
408	efficiencies are very low, with PLQY values in THF being 0.03 and 0.02 for C1 and
409	C2.



410
 411 Fig. 4. (a) - Emission spectra of Me-DBM, CBZ-DBM and their Eu³⁺ complexes C1-C4 in THF solutions (c~1.5·10⁻⁵M); (b) – photograph of Me-DBM, CBZ-DBM and their Eu³⁺ complexes C1-C4 in THF solutions under excitation with 365 nm UV-lamp.

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CBZ-DBM based Eu³⁺ ternary and tetrakis complexes C3 and C4 in THF 415 solutions exhibit quite different emission spectra. In the case of *ternary* complex C3 416 the emission spectra show the characteristic red emission from Eu^{3+} ion and also an 417 emission band ranging from 400 to 600 nm that is attributed to the luminescence of 418 CBZ-DBM. Intensity ratio between emission at 611 and 475 nm are 2:1. It is likely 419 that the incomplete energy transfer process from ligand to Eu^{3+} ion is a reason for 420 such behavior. Similar observations were made for other Eu^{3+} complexes with β -421 diketone ligands containing carbazole groups [17, 19, 28]. PLOY for complex C3 in 422 THF solution is 0.10 and CIE color coordinates (x=0.26; y=0.28) lie in cyan blue 423 region, respectively. Complex C3 is also characterized with, relatively to C1 and C2, 424 short mono-exponential lifetime value (38.88 μ m) for ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of Eu³⁺. In 425 the emission spectra of *tetrakis* complex C4 no characteristic Eu^{3+} ion emission bands 426 are observed and only the emission of the ligand is present. This could be explained 427 with a known tendency of tetrakis complexes to dissociate into tris complexes and the 428

429 corresponding tetraethylammonium salt [29], what could greatly affect the emission
430 intensity of the Eu³⁺ ion and intensify the emission of the ligand.

431 Solid-state photoluminescence properties of the Eu^{3+} complexes are 432 summarized in Table 2 and photoluminescence excitation and emission spectra are 433 shown in Fig. 5.



Fig. 5. (a) – Excitation spectra (λ_{em}=611 nm) of powders of complexes C1-C4; (b) – Emission spectra
(λ_{exc}=400 nm) of C1-C4 powders. (c) Aggregation enhanced emission of the compound C2, illustrated
by UV irradiated solutions with different THF:hexane volume fractions.

In solid powdered state all complexes exhibit wide excitation bands ranging from 300 to even 470 nm with maxima around 400 nm. These wide bands correspond very well to the absorption spectra of the complexes (Fig. 2), therefore confirming assumption that the emission of Eu^{3+} ion arises from the energy that is absorbed by the coordinated ligands. Furthermore, the excitation spectra in solid-state also contains some Eu^{3+} ion excitation bands at 396 (${}^7F_0 \rightarrow {}^5G_4$), 417 (${}^7F_0 \rightarrow {}^5L_6$) and 467 nm (${}^7F_0 \rightarrow {}^5D_3$), which overlap with the much stronger excitation bands of the ligands.

447 Excitation window for four newly synthesized complexes C1-C4 in solid-state have been extended to the visible light region, what can be considered as an advantage, 448 because Eu^{3+} complexes with β -diketones usually show low stability under the UV-449 450 light irradiation.

451

452

453

Table 2

Excitation and emission spectra maximums (λ_{exc} , λ_{em}), absolute photoluminescence quantum yields (PLQY), luminescence lifetimes (τ_1 , τ_2) and intensity ratios I_2/I_1 between transitions ${}^5D_0 \rightarrow {}^7F_2/{}^5D_0$ 454 7 E, of complexes C1-C4 in solid-state and doped PVK films 455

	\rightarrow Γ_1 of complexes C1-C4 in solid-state and doped F VK limits.							
Compound	λ_{exc} , nm	λ_{em} , nm	PLQY	I_2/I_1	τ ₁ , μs	τ ₂ , μs		
C1	399	611	0.53	29.3	431±2 (67%)	157±4 (33%)		
C2	399	611	0.57	29.9	410±1 (68%)	124±2 (32%)		
C3	412	611	0.09	28.1	170±2 (13%)	51±1 (87%)		
C4	398	611	0.10	29.7	191±1 (15%)	48±0.5 (85%)		
C1-PVK	351	611	0.22	31.6	364±1(71%)	116±1(29%)		
C2-PVK	361	611	0.18	27.3	354±1(67%)	104±1(33%)		
C3-PVK	346, 379	611	0.07	22.9	362±17(23%)	93±3 (77%)		
C4-PVK	346, 379	611	0.09	23.4	295±2 (26%)	84±1 (74%)		

456

Upon the excitation with 400 nm, the powders of complexes C1-C2 show only 457 the typical Eu^{3+} ion emission bands, with a significant enhancement in emission 458 efficiency (PLQY = 0.53 and 0.57) in comparison to the measurements in solution. 459 Such behavior strongly infers that these compounds exhibit the aggregation enhanced 460 emission (AEE). Indeed, this effect can be unambiguously demonstrated in the case of 461 C2 in the THF: hexane solvent system, where with an increasing hexane fraction a 462 suspension of the complex particles forms, "turning-on" the bright red emission (Fig. 463 5 (c)). To the best of our knowledge, only one report has attributed aggregation 464 induced emission (AIE) or AEE effects to Eu^{3+} complexes, where the metal was 465 sensitized with tetraphenylethene, a well-known AIE emitter [30]. At the same time, 466 DBM and its close structural analogues, in their complexed state with boron 467 trifluoride, are very well known frameworks for AIE-active compounds [31-34]. So it 468 is not surprising, that the same molecular system, but complexed with Eu³⁺ ion, would 469 exhibit AEE effect. 470

471 Complexes C3 and C4 with CBZ-DBM ligands, which in solution spectra showed the emission of ligand or the combination of emission of ligand and Eu^{3+} ion, 472 in solid-state exhibit only metal centered luminescence. This can be explained by a 473 474 combination of two effects: a stronger bonding between ligand and metal takes place in the solid-state and the emission of the ligand is completely quenched due to the 475 476 aggregation. In comparison to Me-DBM based counterparts, no enhancement is observed in emission efficiency of the C3 and C4. The relatively low PLQY values of 477 these compounds, once more, point to a poor excitation transfer between the ligand 478 and Eu^{3+} ion. 479

Emission spectra of complexes C1-C4 in solid-state contains five typical Eu^{3+} 480 ion emission lines in the range from 575 to 720 nm. Emission band at ~580 nm 481 $({}^{5}D_{0} \rightarrow {}^{7}F_{0})$ shows a weak intensity due to the fact, that its corresponding transition is 482 forbidden by electric dipole and magnetic dipole moments. Unlike in the solution 483 spectra, this transition is not observed as a sharp peak, but rather than a poorly 484 resolved wide band. Transition ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ (594 nm), which is forbidden by electric 485 dipole moment but allowed by magnetic dipole moment, shows two to three Stark 486 components. Emission spectra is dominated by sharp, hypersensitive electric dipole 487 allowed transition at 611 nm $({}^{5}D_{0} \rightarrow {}^{7}F_{2})$ with full half width of ~ 6 nm, likewise it was 488 observed for solution samples. It is known, that electric dipole transitions of 489 lanthanide ions are quite sensitive to ligand field. Usually strongly asymmetric or 490 strongly interacting ligand fields lead to relatively intense electric dipole transitions 491 [35]. In our case the intensity ratio I_2/I_1 between transitions ${}^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ are 492 very high (28.1-29.9), which shows, that not only Eu^{3+} ion is located in a site without 493 an inversion symmetry, but strong coordination interactions also take place. 494 495 Moreover, I_2/I_1 in solid-state is higher than in solutions, pointing to weaker

interactions between ligands and central metal ion in the dissolved state. Similar observations about I₂/I₁ in different states were reported for other Eu³⁺ complexes [36, 37]. Such intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition in comparison to the intensity of other Eu³⁺ emission lines is the reason why emission color of all four complexes is in red region, with CIE x=0.67; y=0.33.

To further understand the photoluminescence behavior, luminescence lifetimes 501 of ${}^{5}D_{0}$ excited state of Eu³⁺ ion were determined by monitoring the transition at 611 502 nm at room temperature. All luminescence decay curves were fitted with bi-503 exponential functions and have two decay time values τ_1 and τ_2 (Table 2). Bi-504 exponential lifetimes point to the presence of two sites of symmetry around central 505 metal ion. This hypothesis is confirmed by the relatively broad emission of ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ 506 transition, observed at 580 nm. The splitting of the bands, marking this transition in 507 photoluminescence spectra, points to different non-equivalent sites in Eu^{3+} complexes 508 [38]. In solid-state the distance between two emitting Eu^{3+} ion sites are relatively 509 short and the interaction between Eu^{3+} - Eu^{3+} centers can take place. Multiple 510 aggregated forms of the compound with alternative local chemical environments 511 would lead to species with different emission kinetics. Bi-exponential lifetime in 512 solid-state were also reported for other Eu³⁺ ternary and tetrakis complexes [25, 37, 513 39, 40]. As it is the case for PLQY, lifetime values are not greatly affected by the 514 structure of complexes (*ternary* or *tetrakis*) and τ_1 and τ_2 values vary in the range 515 from 3 to 33 μ s, if the same ligands are present. 516

517

3.4. Eu³⁺ complex behavior in host materials and OLEDs

The incorporation of Eu^{3+} complexes in practically applicable devices often involves a use of guest-host systems, where the emitting molecule is dispersed in polymeric or molecular matrix. This has to be done in order to improve optical

521 transparency and ensure plasticity to the initially crystalline materials. Additionally, a host material with charge transporting properties is a necessity in order to acquire 522 efficient OLEDs with Eu^{3+} based emitters [10, 11]. To investigate the effects of 523 dispersion in polymer matrix, the synthesized compounds were dispersed in a 524 conventional hole-transporting material, poly(N-vinylcarbazole) (PVK). Four PVK 525 films doped with 8 weight percent (wt%) of complexes C1-C4 were prepared by spin 526 coating technique from THF solutions. 527



528 529

Fig. 6. Emission spectra of PVK films doped with 8 wt% of complexes C1-C4. Emission spectra of doped PVK films are shown in Fig. 6 and the relevant 530 emission data (PLOY, τ_1 and τ_2) are collected in Table 2. When excited at 380 nm, all 531 doped films exhibit only characteristic Eu^{3+} ion emission bands in the red-light region 532 and no emission from PVK are detected in shorter wavelengths. The films with 533 complexes C1 and C2 exhibit moderate PLQY of 0.22 and 0.18, but complexes C3 534 and C4 - 0.07 and 0.09. These values give an important insight about the differences 535 in the emission characteristics between the two subsets of compounds. The dispersion 536 in polymer matrix causes a drop in PLQY by more than 50% for Me-DBM based 537

538 complexes, while CBZ-DBM shows no significant change in comparison to the emission efficiency in the powdered form. This difference in the behavior can be 539 explained by the fact that C1 and C2 exhibits an AEE effect, while the emission of 540 541 C3 and C4, apparently, is not affected by a solid state packing arrangement. The dispersion in polymer can be considered as a pseudo-solvation, where molecules are 542 encapsulated by the host material. However, for solution-processed guest-host 543 systems, unless the polar guest is completely encapsulated by isolating groups, a large 544 portion of the dispersed molecules still forms aggregates [41]. This is an explanation 545 for the PLOY drop for guest-host systems of C1 and C2, where only the aggregated 546 fraction of the molecules emit, while the emission in the isolated molecules is 547 quenched. In C3 and C4 the both fractions of the molecules are able to emit, hence no 548 549 apparent change in PLQY is observed.

Regarding the discussed difference between the emissive properties of Me-DBM 550 and CBZ-DBM based compounds, it can be attributed to the dissimilar electronic 551 552 nature of these ligands. It is known that AIE and AEE effects largely take place due to the restriction of the emission-quenching intramolecular rotation, when the molecules 553 are packed in crystal lattice [42]. In Me-DBM this rotation, most likely, can be related 554 to the torsion changes between phenyl ring and diketone fragment. As discussed 555 previously, in **CBZ-DBM** the lowest energy electronic transition has CT character 556 that involves the push-pull system consisting of carbazole electron donating group 557 and diketone acceptor. As it is well known, the conjugation energy in push-pull 558 molecules causes their planarization and reduces conformational freedom. This can be 559 considered as the reason why the compounds based on CBZ-DBM do not exhibit 560 AEE effect and this ligand is strongly emissive in solution, while Me-DBM does not 561 562 emit.

563 In order to evaluate a possible enhancement in solid-state emission quenching for **CBZ-DBM** based compounds, PLQY for this ligand in a host-free film was 564 measured, yielding a value - 0.05. While a steep drop in PL efficiency can be seen for 565 **CBZ-DBM** in comparison to solution, indicating a strong concentration quenching, 566 solid phase emission efficiency notably increases for CBZ-DBM based Eu³⁺ 567 complexes. In addition, PLOY of C3 and C4 is almost identical in host-free and PVK-568 dispersed samples, showing no significant concentration dependence. These 569 observations let assume that, while **CBZ-DBM** is highly susceptible to photoinduced 570 electron transfer quenching, this effect is suppressed by the complexation to Eu^{3+} . 571 This can be explained by a fast excited state migration to the metal center, which is 572 573 sterically encapsulated by the ligands.

Taking into the consideration the previously discussed results, two OLEDs 574 were prepared containing complex C1 as the emitter, where this compound was either 575 **PVK** [ITO/PEDOT:PSS(40nm)/PVK:C1(50nm)(10wt%)/ dispersed in host 576 TPBi(20nm)/LiF(1nm)/Al(100nm)] or used in a host-free layer [ITO/PEDOT:PSS 577 (40nm)/C1(50nm)/TPBi(20nm)/LiF(1nm)/Al(100nm)]. In the presence of the host 578 material no characteristic Eu^{3+} emission band was observed in the spectra of the 579 580 device, as it emitted only blue light, associated with the electroluminescence (EL) of the charge transporting compounds. On the other hand, the host-free OLED showed 581 only red Eu^{3+} related emission. The lack of the host and the poor charge transporting 582 characteristics of the compound determines that the device exhibits low maximal 583 brightness of 10 cd/m^2 , with current efficiency 0.004 cd/A and turn-on voltage 9 V. 584 These results reaffirm that due to AEE effect the ability to emit is greatly reduced for 585 Me-DBM based complexes, as they are dispersed in host material. 586

587

588 **3.5. Energy transfer between ligands and Eu³⁺ ion**

To better understand the observed partial and complete energy transfer 589 between ligands **CBZ-DBM** or **Me-DBM** and Eu³⁺ ion, the singlet and triplet excited-590 state energy levels were determined experimentally in the case of CBZ-DBM and 591 using the ORCA quantum chemical calculation program in the case of Me-DBM. A 592 simplified energy transfer process between ligands and Eu^{3+} ion can be expressed as a 593 following exited state transition sequence: S_1-T_1 -Eu*. First, energy from the excited 594 singlet state (S_1) of ligand is transferred to its excited triplet state (T_1) . Second, energy 595 from T₁ state is transferred onto the excited states of the Eu³⁺ ion (usually ${}^{5}D_{0}$). Some 596 authors have proposed interaction mechanisms involving these energy states to 597 evaluate the effectiveness of the excitation transfer process: (1) Reinhoudt empirical 598 rule [43] states, that for an efficient transfer between S_1 - T_1 levels, the energy 599 difference between these two states should be around 5000 cm^{-1} ; (2) however, for 600 effective energy transfer between T_1 -Eu*, the difference needs to be in the range 601 2500-5500 cm⁻¹ (Latva empirical rule) [44]. 602

For ligand Me-DBM singlet and triplet energy levels are located at 28 218 and 603 21 928 cm⁻¹, and for ligand **CBZ-DBM** at 21 929 and 18 416 cm⁻¹, respectively (Fig. 604 7). All calculated energy levels are higher than the ${}^{5}D_{0}$ energy level of Eu³⁺ ion (17) 605 250 cm⁻¹). In the case of Me-DBM ligand, the difference between levels S_1-T_1 is 606 6290 cm⁻¹ and T₁-Eu^{*} – 4678 cm⁻¹. This means that the both empirical rules 607 discussed previously are fulfilled and the energy transfer process is efficient. High 608 emission PLQY values in the solid-state for complexes C1 and C2 confirms this 609 statement. For ligand **CBZ-DBM** the situation is different and the obtained energy 610 gap values for S_1-T_1 and T_1 -Eu* are smaller than those for Me-DBM – 3513 and 611 1166 cm⁻¹, respectively. The difference between the excited singlet and triplet energy 612

states of CBZ-DBM is less than 5000 cm⁻¹, what could indicate a non-efficient 613 intersystem crossing in this molecule. This is probably the reason, why the emission 614 of the ligand is also observed in the luminescence spectra of complexes C3 and C4 in 615 THF solutions. Not all energy from S₁ level is transferred to T₁ level and some part of 616 it manifests as the ligand fluorescence. Furthermore, energy difference between triplet 617 state of **CBZ-DBM** and ${}^{5}D_{0}$ energy level of Eu³⁺ ion is notably lower than the 618 preferable value $(2500-5500 \text{ cm}^{-1})$ -[43]. In the cases, where the gap is less than 3500 619 cm⁻¹, the energy back-transfer from ${}^{5}D_{0}$ energy level of Eu³⁺ ion to T₁ level of the 620 ligand could occur. This is another likely cause for the low PLQY values of CBZ-621 **DBM** based complexes. 622



Fig. 7. Schematic energy level diagram of energy transfer processes: Me-DBM-to-Eu³⁺, CBZ-DBM-to-Eu³⁺, CBZ-DBM-to-

energies, therefore secondary ligand PHEN can transfer absorbed excited energy not only directly to resonance level (${}^{5}D_{0}$) of Eu $^{3+}$ ion, but also to S₁ and T₁ levels of ligands **CBZ-DBM** and **Me-DBM**.

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636 4. CONCLUSIONS

Two β-diketones with methyl and carbazole substituents attached to dibenzoylmethane (**Me-DBM**, **CBZ-DBM**) and their corresponding novel Eu^{3+} *ternary* (Eu(Me-DBM)₃PHEN **C1**, Eu(CBZ-DBM)₃PHEN **C2**) and *tetrakis* ([Eu(Me-DBM)₄]N⁺(Et)₄ **C3**, Eu(CBZ-DBM)₄]N⁺(Et)₄ **C4**) complexes were synthesized, fully characterized with ¹H NMR, ¹³C NMR, FT-IR spectroscopy methods, elemental analysis and thermogravimetric analysis.

The photophysical properties of the compounds were investigated in solution 643 and solid-state. The acquired results show that the complexes based on Me-DBM 644 ligand exhibit strong AEE behavior, with very low emission efficiency in solutions 645 and moderately high PLQY values of 0.53 and 0.57 in powders. CBZ-DBM based 646 complexes in solution show either dual Eu^{3+} and ligand centered emission (C3) or 647 only ligand emission (C4), while in the solid state only Eu^{3+} emission is detected. At 648 the same time the measured solid-state PLQY values of **CBZ-DBM** based compounds 649 are notably lower (0.09 and 0.10). The results of quantum chemical modeling show 650 that this decrease in luminescence efficiency is mainly attributed to the close situated 651 S_1 and T_1 energy levels of **CBZ-DBM** that obstruct the intersystem crossing process. 652 Additionally, no AEE behaviour was observed for C3 and C4 due to CT nature of 653 **CBZ-DBM** that reduces the conformational freedom of the molecule. 654

Taking into account the practical application aspects of the synthesized compounds, the molecular design of **Me-DBM** based complexes can be considered as

more promising, due to increased emission efficiency. AEE characteristics of these compounds can be exploited towards the development of environment-sensitive luminescent probes. The potential use of these compounds in OLEDs is limited due to the fact that the dispersion in charge transporting host reduces emission efficiency through the obstructed aggregation ability of the molecules.

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Highlights

- Eu-complexes with 4-methyl- and 4-carbazol-9-yl-dibenzoylmethane ligands are shown.
- In solution Eu^{3+} ternary complex with carbazole β -diketone show dual emission.
- Eu-complexes with carbazole β -diketones show partial energy transfer process.
- Eu-complexes with methyl β -diketone exhibit aggregation enhanced emission.
- OLED containing Eu-complexes with methyl β -diketone show brightness of 10 cd/m².