

Self-organization of chiral self-complementary europium complex with a new achiral tripod-type ligand: Synthesis and stereochemistry effects to complex luminescence properties

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Abstract

Solid complexes of europium picrate with the ligands: 2-(bis-dibutylcarbamoylmethyl-amino)-*N,N*-dibutyl-acetamid (L_1), 2-{bis-[(ethyl-phenyl-carbamoyl)-methyl]-amino}-*N*-ethyl-*N*-phenyl-acetamide (L_2) and 2-(bis-diethylcarbamoyl methyl-amino)-*N,N*-diethyl-acetamide (L_3) were prepared and characterized by elemental analysis, conductivity measurements and IR spectra. For the $[\text{Eu}(\text{pic})_3L_1]$, X-ray measurements show that the screw coordination arrangement of the achiral tripod-type ligand (L_1) around the Eu(III) ion induces the chirality of clockwise (*C*) and anticlockwise (*A*) molecular structures. And, the luminescence properties of tripod-type ligands with Eu(III) ion were affected by the complex stereochemistry.

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1. Introduction

Since the historic discovery of spontaneous resolution in ammonium sodium tartrate by Louis Paster, chirality has been an important topic in chemistry, pharmacy, and living organisms. Chirality was expressed at the molecular and supramolecular levels [1–5]. The initial progress in chirality was in the generation of molecular chirality from the reaction of achiral components, which developed into assembling isolated chiral molecules [6]. Although the law of physics under specific conditions determines the formation of chiral molecules, these laws are not yet fully understood [7]. To realize the synthetic strategy, we have focused on metal complexes with tripod-type ligands, because the coordination bonding interactions is regarded as the most important driving forces in generating chiral compounds.

To investigate the self-organization of chiral self-complementary lanthanide complexes with achiral tripod-type ligands and the stereochemistry effects on complex luminescence properties, the europium(III) complexes of three tripod-type ligands involving different terminal groups with the formulas $[\text{Eu}(\text{pic})_3L_1]$ (**1**), $[\text{Eu}(\text{pic})_3L_2]$ (**2**) and $[\text{Eu}(\text{pic})_3L_3]$ (**3**) were synthesized, where $L_1 = 2$ -(bis-dibutylcarbamoylmethyl-amino)-*N,N*-dibutyl-acetamide, $L_2 = 2$ -(bis-[(ethyl-phenylcarbamoyl)-methyl]-amino)-*N*-ethyl-*N*-phenyl-acetamide and $L_3 = 2$ -(bis-diethylcarbamoylmethyl-amino)-*N,N*-diethyl-acetamide.

2. Experimental

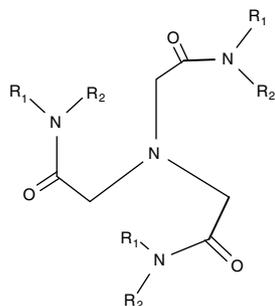
2.1. Materials

All the chemical reagents used in this work were analytical grade. The europium picrate salt [8] and L_{1-3} [9,10] were prepared according to literature methods.

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2.2. Chemical and physical measurements

The metal ions were determined by EDTA titration using xylenol orange as an indicator. C, N and H were determined using an Elementar Vario EL instrument. IR spectra were recorded on a Nicolet Avatar 360 FT-IR instrument using KBr discs in the 400–4000 cm^{-1} region. Conductivity measurements were carried out with a DDSJ-308 type conductivity bridge using 10^{-3} mol dm^{-3} solutions in acetone at 25 °C. Luminescence measurements were made on a Hitachi F-4500 spectrofluorophotometer equipped with quartz cures of 1 cm path length. The excitation and emission slit widths were 5.0 nm. Time-resolved fluorescence measurements were performed at 77 K using a Nd-YAG pumped dye laser with RG 10 dye as the excitation source and a Spex 1403 double grating monochromator. X-ray measurements were performed on a P4 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation at 293 K, using the $\omega/2\theta$ scan mode. Lorentz and polarization corrections were applied, and empirical absorption correction was made. A summary of crystallographic data and details of the structure refinement are listed in Table 1. The structure was solved by



L₁: R₁, R₂ = butyl
L₂: R₁ = phenyl, R₂ = ethyl
L₃: R₁, R₂ = ethyl

direct methods and refined by full-matrix least-square techniques with all nonhydrogen atoms treated anisotropically. All calculations were performed on an Eclipse S/140 computer with the program package SHELXTL [11] version 5.10.

2.3. General preparation of 1, 2 and 3

1: Solution of 2-(bis-dibutylcarbamoylmethyl-amino)-*N,N*-dibutylacetamide (L₁) (0.2 mmol, in 10 ml of ethanol) was added dropwise to the solution of europium picrate salt (0.2 mmol, in 5 ml of ethanol). The mixture was stirred at room temperature for 8 h. The yellowish precipitated solid complex was filtered, washed with ethanol three times and dried in vacuo over P₄O₁₀ for 48 h. The solid **1** was recrystallized from CH₃OH solution by slow evaporation

Table 1
Crystal data and structure refinement for the complex [Eu(pic)₃L₁]

Empirical formula	C ₄₈ H ₆₆ N ₁₃ O ₂₄ Eu
Temperature (K)	293
Crystal color	Yellow
Crystal size (mm ³)	0.20 × 0.20 × 0.30
Formula weight	2738.22
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimension	
<i>a</i> (Å)	23.2890 (10)
<i>b</i> (Å)	19.8820 (10)
<i>c</i> (Å)	28.9870 (2)
α (°)	90
β (°)	112.690 (10)
γ (°)	90
<i>V</i> (Å ³)	12383.1 (15)
<i>Z</i>	4
Density (calculated) (g/cm ³)	1.469
<i>F</i> (000)	5636
Radiation, graphite-monochromatized, λ (Å)	0.71073
μ (Mo $K\alpha$) (cm ⁻¹)	1.101
θ Range for data collection	1.80–27.00
<i>R</i> (all data)	<i>R</i> ₁ = 0.0577, <i>wR</i> ₂ = 0.1610 ^a
Largest difference peak and hole [e Å ⁻³]	−1.17, 1.51

$$^a w = 1/[\sigma^2(F_o)^2 + (0.0800p)^2 + 1.9500p] \text{ where } p = (F_o^2 + 2F_c^2)/3.$$

to give transparent yellowish crystals. Yield: 87%. m.p. 73 °C. Anal. data, calc. for C₄₈H₆₆N₁₃O₂₄Eu: C, 42.36; H, 4.89; N, 13.38; Eu, 11.17. Found: C, 41.96; H, 4.53; N, 13.16; Eu, 11.35. Main IR (cm⁻¹): 1613 ($\nu_{\text{C=O}}$), 1275 ($\nu_{\text{C-O}}$), 1576, 1544 ($\nu_{\text{as-NO}_2}$), 1362, 1324 ($\nu_{\text{s-NO}_2}$) (KBr) Table 2.

2 was prepared in the similar manner except 2-[[ethyl-phenyl-carbamoyl]-methyl]-amino}-*N*-ethyl-*N*-phenylacetamide (L₂) was used. Yield: 91%. m.p. 89 °C. Anal. data, calc. for C₄₈H₄₂N₁₃O₂₄Eu: C, 43.12; H, 3.17; N, 13.62; Eu, 11.37. Found: C, 43.23; H, 3.33; N, 13.51; Eu, 11.61. Main IR (cm⁻¹): 1615 ($\nu_{\text{C=O}}$), 1278 ($\nu_{\text{C-O}}$), 1576, 1542 ($\nu_{\text{as-NO}_2}$), 1365, 1323 ($\nu_{\text{s-NO}_2}$) (KBr).

Table 2
Selected bond lengths (Å) and bond angles (°) for [Eu(pic)₃L₁] (**1**)

Eu(1)—O(1)	2.383 (4)	Eu(2)—O(28)	2.424 (6)
Eu(1)—O(2)	2.373 (4)	Eu(2)—O(29)	2.348 (6)
Eu(1)—O(3)	2.455 (4)	Eu(2)—O(30)	2.389 (6)
Eu(1)—O(4)	2.373 (4)	Eu(2)—O(31)	2.394 (5)
Eu(1)—O(5)	2.627 (4)	Eu(2)—O(37)	2.601 (7)
Eu(1)—O(11)	2.320 (4)	Eu(2)—O(38)	2.250 (6)
Eu(1)—O(17)	2.604 (4)	Eu(2)—O(45)	2.307 (7)
Eu(1)—O(18)	2.293 (4)	Eu(2)—O(46)	2.690 (6)
Eu(1)—N(4)	2.770 (4)	Eu(2)—N(17)	2.742 (4)
Eu(1)—N(4)—C(1)	110.14 (4)	Eu(2)—N(17)—C(49)	99.75 (5)
Eu(1)—N(4)—C(3)	105.92 (4)	Eu(2)—N(17)—C(51)	110.04 (5)
Eu(1)—N(4)—C(5)	106.28 (4)	Eu(2)—N(17)—C(53)	110.85 (5)
N(4)—C(1)—C(2)	115.92 (7)	N(17)—C(49)—C(50)	116.91 (8)
N(4)—C(3)—C(4)	112.50 (7)	N(17)—C(51)—C(52)	112.28 (7)
N(4)—C(5)—C(6)	114.39 (7)	N(17)—C(53)—C(54)	119.44 (8)

3 was prepared as similar to **1** and **2** except 2-(bis-diethylcarbamoylmethyl-amino)-*N,N*-diethyl-acetamide (L_3) was used. Yield: 78%. m.p. 86 °C. Anal. data, calc. for $C_{36}H_{42}N_{13}O_{24}Eu$: C, 36.25; H, 3.55; N, 15.27; Eu, 12.74. Found: C, 36.21; H, 3.50; N, 15.21; Eu, 12.53. Main IR (cm^{-1}): 1611 ($\nu_{C=O}$), 1273 (ν_{C-O}), 1577, 1540 (ν_{as-NO_2}), 1362, 1321 (ν_s-NO_2) (KBr).

3. Results and discussion

3.1. Properties of the complexes

Analytical data for the complexes conform to a 1:3:1 metal-to-picrate-to- L stoichiometry [$Eu(pic)_3L_{1-3}$]. All complexes are soluble in DMSO, DMF, THF, $CHCl_3$, CH_3CN , methanol and acetone, ethyl acetate, and sparingly soluble in benzene, Et_2O and cyclohexane. Conductivity measurements for these complexes in acetone solution indicate that three complexes are nonelectrolytes, implying that all of the picrate groups coordinate to Eu(III) in each complex [12].

3.2. IR spectra

Free L_{1-3} show band at about 1642 cm^{-1} which may be assigned to $\nu(C=O)$. In the IR spectra of complexes, the bands of $\nu(C=O)$ of free L_{1-3} shift about $27\text{--}31\text{ cm}^{-1}$ towards lower wave numbers, indicating the C–O groups take part in coordination to the metal ions. The OH out-of-plane bending vibration of the free Hpic at 1151 cm^{-1} disappears, indicating that the H-atom of the OH group is replaced by Eu(III). The vibration $\nu(C-O)$ of the Pic[−] at 1265 cm^{-1} is shifted toward higher frequency by $8\text{--}13\text{ cm}^{-1}$ in the complexes. This is due to the following two effects. First, the hydrogen atom of the OH group is replaced by Eu(III), increasing the π -bond character in the C–O bond. Secondly, coordination of the nitrogen atom of L –Eu(III) decreases the π -character [13]. Furthermore, the characteristic frequencies ($1342, 1555\text{ cm}^{-1}$) of free picrate were divided into two double peaks (about $1362, 1325$ and $1576, 1545\text{ cm}^{-1}$, respectively), indicating that the picrate groups coordinate to the metal ions as bidentate ligands [14].

3.3. X-ray crystal structure

The molecular structures and schematic representations of **1** were shown in Fig. 1, and revealed that each Eu center binds to one nitrogen atom and three oxygen atoms from the ligand L_1 and five oxygen anions from picrate groups where one picrate group is monodentate and the remaining two are bidentate. The complex induces the chirality of C and A structures due to the screw coordination arrangement of the achiral tripod-type ligand. The values of the angles formed by the monodentate picrate group and the center europium ion are different indicating that structures C and A are not enantiomers. In structure C , the torsion

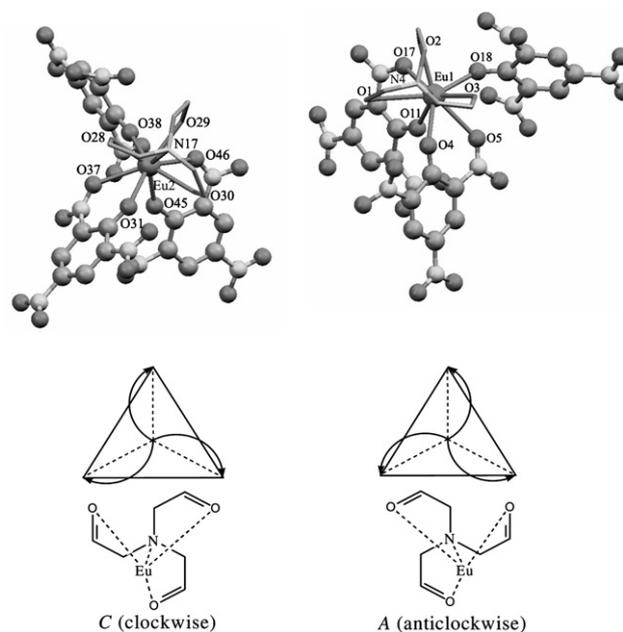


Fig. 1. Molecular structures of the C (left) and A (right) and their schematic representations, in which the curve line from the central tertiary amine to the coordination oxygen atom through the methylene is represented by the arrow. The dibutyl groups have been omitted for clarity.

angles of $N(17)\text{--}C(49)\text{--}C(50)\text{--}O(28)$, $N(17)\text{--}C(51)\text{--}C(52)\text{--}O(29)$, and $N(17)\text{--}C(53)\text{--}C(54)\text{--}O(30)$ are 22.82° , 20.31° and 16.46° . While in structure A , the torsion angles of $N(4)\text{--}C(1)\text{--}C(2)\text{--}O(1)$, $N(4)\text{--}C(3)\text{--}C(4)\text{--}O(2)$ and $N(4)\text{--}C(5)\text{--}C(6)\text{--}O(3)$ are -5.17° , -27.44° and -10.21° , respectively.

The complex packing diagram shows that the C and A structures coexist in the crystal. There is no intermolecular hydrogen-bond extended structure. In the crystal lattices of the picrate salt complex (L_1), the picrate ions are located in the cavities, and the homochiral layer consisting of C structures and the adjacent layer consisting of A structures are well stacked by adopting the up-and-down layer's shape to give a 2D double-layer structure $\dots CCCC\dots$ and $\dots AAAAA\dots$ (Fig. 2). The similar structure of magnesium complex with tripod-type ligand have been reported by He [15]. Three chains of ligand have two different rounding directions: C (clockwise) and A (anti clockwise). And, the C and A structures coexist in the unit cell Fig. 3.

3.4. The luminescence properties of the complexes

To investigate the influences of the complex fluorescence by coordination stereochemistry, L_2 , L_3 and their europium complexes were synthesized by the same methods. L_{1-3} form the 1:3:1 (ligand-to-picrate group-to-europium ion) complex with Eu(III) ion where L_{1-3} act as tetradentate ligands, the remaining coordination sites are occupied by picrate groups that could absorb light at $\lambda = 437\text{ nm}$ and transfer energy to Eu(III) ion inducing the europium characteristic emission at $\lambda = 578, 591$ and 614 nm . This

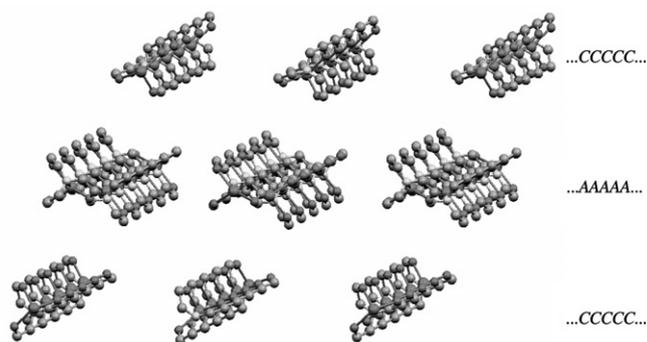


Fig. 2. The packing diagram of **1** showing that the *C* and *A* are arrayed in an up-and-down fashion to give a 2D double-layer structure (...CCCCC..., ...AAAAA... and ...CCCCC...). The synergistic picrate groups and the terminal dibutyl groups have been omitted for clarity.

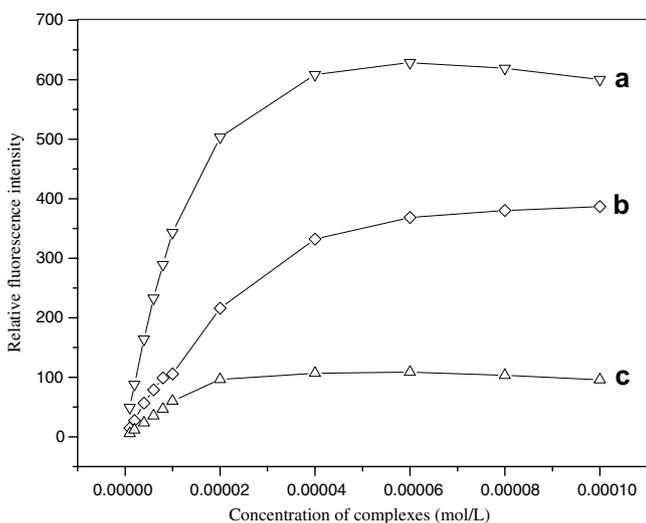
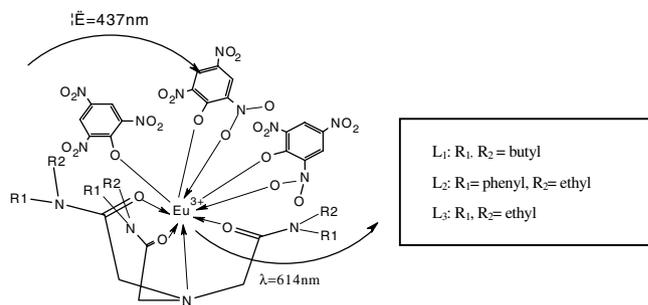


Fig. 3. The relative luminescence intensity of complexes in CHCl_3 solutions with different concentrations. (a) **1**, (b) **2**, (c) **3**. The progressive concentration of complexes induced a progressive increase in the luminescence intensity at $\lambda = 614 \text{ nm}$. But a small quenching of complexes luminescence is observed when the concentration reached about $6 \times 10^{-5} \text{ mol/L}$. This behavior is ascribed to the intermolecular dynamic quenching *via* energy transfer, and was found to obey strictly the Stern–Volmer relationship along the investigated concentration range (up to $5 \times 10^{-5} \text{ mol/L}$) [18].

behavior can be explained considering that: (3) the tripodal ligands L_{1-3} impose a trigonal cavity-like stereochemistry on the Eu(III) ion, leaving vacant axial positions. (33) the oxygen anions of three picrate acids occupy these vacant positions and transfer electronic energy to Eu(III) ion. (333) L_{1-3} coordinate to the metallic site and prevent the attack from solvent molecules. Scheme 1. shows the mechanism of producing the europium characteristic luminescent. Contrast to common series of tetramine ligands, L_{1-3} have only one $-\text{CH}_2-$ between the apex nitrogen atom and amide group that reducing the size of cavities among three coordination chains, which improve the ligand ability to protect the metal center from attacking by solvent molecules. To limit the quenching of Eu(III) luminescence by



Scheme 1. The picrate groups are fluorophores of the complexes which absorb light at $\lambda = 437 \text{ nm}$ and induce the europium characteristic emission.

high-frequency N–H oscillators in the final europium complex [16], three secondary amines have been introduced into the ligand skeletons, which are then transformed into tertiary amide connectors in complexes [17].

The terminal group effects of luminescence properties were investigated by contrasting the luminescence intensity of **1** with its derivatives (**2** and **3**). Compound **1** exhibits about 60-fold luminescence intensity to that of **3** due to its terminal substituent group's flexibility and size. For L_1 , L_2 and L_3 , the flexibility in the order of $L_2 < L_3 < L_1$ and the size of space that the terminal groups occupied in the order of $L_3 < L_1 < L_2$. The stereochemistry differences of three terminal groups in final complexes lead to different luminescence intensity due to their abilities in protecting europium ions from quenching by high-energy vibration molecules. These behaviors were also in good agreement with the results obtained from measuring the luminescence lifetimes of the complexes (τ_1 : 0.45 ms, τ_2 : 0.42 ms, τ_3 : 0.17 ms, Fig. 4).

4. Summary and conclusions

In summary, the complex **1** induces the chirality of *C* and *A* structures due to the screw coordination arrangement of the achiral tripod-type ligand and in the unit cell, the homochiral layer consisting of *C* structures and the adjacent layer consisting of *A* structures are well stacked by adopting the up-and-down layer's shape to give a 2D double-layer structure ...CCCCC... and ...AAAAA... Tripodal ligands are able to shield the encapsulated Eu^{3+} from interaction with the surroundings, and the introduction of more flexible and larger terminal substituents disfavours the solvent molecule's coordination to center Eu(III) ions whose intermolecular energy transfer quench the complex luminescent.

5. Supplementary data

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 214441. Copies of this information may be obtained free of charge from the

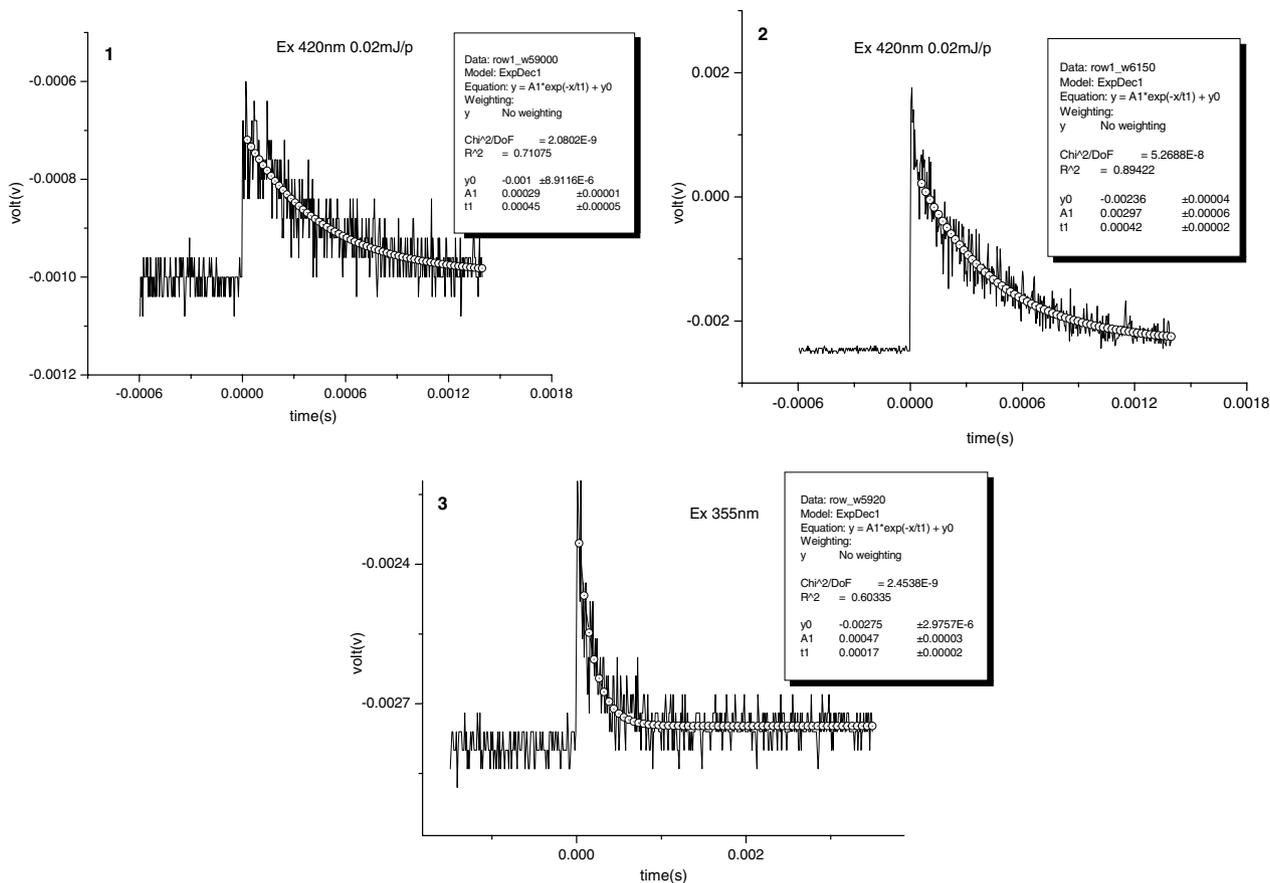


Fig. 4. The fluorescence lifetime of **1**, **2** and **3**. τ_1 : 0.45 ms, τ_2 : 0.42 ms, τ_3 : 0.17 ms.

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