

# The influence of the structure of pyromellitic acid on the luminescence intensity of graphene oxide/rare earth complexes hybrid materials

Xiaoxiong Zhang

Hebei University of Engineering

wenjun zhang (✉ [wjzhang@hebut.edu.cn](mailto:wjzhang@hebut.edu.cn))

Hebei University of Technology <https://orcid.org/0000-0002-2815-754X>

Hui Dong

Hebei University of Engineering

Qianqian Liu

Hebei University of Technology

---

## Research Article

**Keywords:** pyromellitic acid, graphene oxide, rare earth complexes,  $\pi$ - $\pi$  stacking, luminescent intensity

**Posted Date:** February 12th, 2021

**DOI:** <https://doi.org/10.21203/rs.3.rs-213839/v1>

**License:**   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

---

**Version of Record:** A version of this preprint was published at Journal of Inorganic and Organometallic Polymers and Materials on March 19th, 2021. See the published version at <https://doi.org/10.1007/s10904-021-01962-x>.

# Abstract

The development of graphene oxide/rare earth complexes luminescent materials is limited due to the strong quenching ability of graphene oxide. However, the hybrid materials with pyromellitic acid (PMA) as ligand not only have better performance, but also have stronger luminescence intensity. Herein we tested the effect of the carboxylic acid structure of PMA on the luminescence intensity of graphene oxide/rare earth complexes hybrid materials. Phthalic acid (PA), Isophthalic acid (*i*-PA) and Terephthalic acid (*p*-PA) are selected as test ligand, representing the o-position, meta-position and para-position effects of PMA. By comparing the luminescence intensity, we found that o-position effect is helpful for the ligand to sensitize rare earth ions, and meta-position and para-position effects are helpful for the graphene oxide sheets (GOSs) to improve the luminescence intensity of hybrid materials and inhibit the quenching effect of the GOSs. Furthermore, we speculate on the relationship between the distance of  $\pi$ - $\pi$  stacking of GOSs and rare earth complexes and luminescence intensity of hybrid materials. This work provides an important reference for the design of graphene oxide/rare-earth aromatic carboxylic acid hybrid luminescent materials.

## 1. Introduction

Graphene, a unique two-dimensional material with excellent physical and chemical properties, shows broad application prospects in the fields of microelectronics, functional materials, chemical sensing, et al. [1–5] However, the preparation of pure graphene monolayer is very difficult and expensive.[6] In practice, graphene derivatives such as graphene oxide or reduced graphene oxide are mainly used to replace pure graphene monolayer. This is mainly due to the advantages of the method of preparing graphene derivatives, such as simplicity, low cost and mass production.[7] In addition, a large number of oxygen-containing functional groups were introduced into the surface of these graphene derivatives, which provided an opportunity for functionalized graphene and the regulation of graphene properties. These active oxygen-containing functional groups can react in the form of covalent bonds or non-covalent bonds to realize the functionalization of graphene and the synthesis of composite materials. At present, graphene oxide has formed various functional composites with semiconductor nanoparticles, metal nanoparticles, organic small molecules and polymers.[8] These materials show great potential applications in battery, supercapacitor, photocatalysis, photovoltaic and other fields.[9–11] In terms of luminescent materials, the  $sp^2$  domain of graphene oxide can quench the luminescent groups, such as dye molecules, conjugated polymers and quantum dots, via fluorescence resonance energy transfer.[12] It greatly limits the application of graphene oxide in luminescent materials. How to solve this problem has become the key to promote the application of graphene oxide in the field of luminescence.

Recently, some graphene oxide/rare-earth hybrid luminescent materials are synthesized by the non-covalent interaction of GOSs and 1,10-Phenanthroline monohydrate (Phen).[13–19] The existence of GOSs not only does not quench the fluorescence of the hybrid materials, but also improves the properties of the hybrid materials, such as improving thermal stability, prolonging fluorescence lifetime and improving quantum efficiency. As for luminescence intensity, GOSs cause different degrees of influence.

The luminescent intensity of most hybrid materials decreases, which is consistent with the quenching mechanism of graphene. In particular, the hybrid material with PMA as ligand even improve the luminescence intensity of the hybrid material.[17] It is not clear what causes this phenomenon. Is it derived from the special aromatic carboxylic acid structure of PMA? PMA has four aromatic carboxylic radicals, which have the structural properties of PA, *i*-PA and *p*-PA respectively. Does this special structure affect the luminescence intensity of hybrid materials?

Based on the above guess, in this work, we choose PMA, PA, *i*-PA and *p*-PA as the first ligand, Phen as the second ligand, and equal amount of graphene oxide dispersions to synthesize hybrid materials. By comparing their luminescent intensity, we hope to find out the special role of PMA, which will be of great significance for the synthesis of novel graphene oxide rare earth luminescent materials.

## 2. Experimental Section

### 2.1 Materials and Instruments

Natural flake graphite was purchased from Qingdao Jinrilai graphite Corporation. Hydrogen peroxide (30%), anhydrous ethanol and Potassium permanganate were issued by Tianjin Jiangtia Chemical Corporation. Pyromellitic acid, phthalic acid, isophthalic acid, terephthalic acid and 1,3,5-benzenetricarboxylic acid (BTC) were recruited from Aldrich. 1,10-Phenanthroline monohydrate was bought from Tianjin Hengshan Chemical Corporation. All the solvents and reagents (analytical grade) were obtained commercially and used without further purification.

Fourier Transform infrared spectroscopy (FT-IR) were registered in a Bruker Ten-sor27 Spectrometer (Germany) with a KBr disc in the wavelength range of  $4000 - 400 \text{ cm}^{-1}$ . The X-ray diffraction (XRD) measurements of the powder samples were carried out by using a Bruker D8 diffractometer (40 mA, 40 kV) with monochromated Cu-Ka1 radiation. The morphology of graphene oxide was investigated using Metallurgical microscope (Phoenix Optical Group Corporation). Fluorescence excitation and emission spectra were recorded on a Hitachi FL-4600 fluorescence spectrophotometer using a 150 W xenon lamp as the excitation source.

### 2.2 Preparation of GOSs

Graphite oxide (GO) is prepared by a modified Hummers method according to our previous reports.[20–21] In a 250 mL flask, 1 g of natural flake graphite, 0.5 g of sodium nitrate and 23 mL of concentrated  $\text{H}_2\text{SO}_4$  were added respectively. After stirring for 30 minutes at  $5^\circ\text{C}$ , 3 g of  $\text{KMnO}_4$  was slowly added within 20–30 minutes. Then, the system was heated for 30 min at  $35^\circ\text{C}$ , 50 mL of distilled water was added gradually, and the mixture was stirred for 15 min at  $98^\circ\text{C}$ . Finally, the mixture was diluted with 140 mL of distilled water and approximate 10 mL 30% of  $\text{H}_2\text{O}_2$  solution, the color of the mixture changed to a luminous yellow. The mixture centrifuged and washed with 500 mL of 5% HCl aqueous solution and distilled water. The product was dried at  $50^\circ\text{C}$  for 24 h. GOSs dispersions (1mg/mL) were obtained by

ultrasonic stripping for the next experiment. 0.1 g of graphite oxide was dispersed in 100 mL anhydrous ethanol and sonicated for 1 h.

## 2.3 Synthesis of graphene oxide/rare-earth aromatic carboxylic acid hybrid materials

In a typical experiment, equal amount of GOSs (5 mg) were used to synthesize graphene oxide/rare-earth aromatic carboxylic acid hybrid materials (named as Eu-PMA-Phen/GOSs, Eu-PA-Phen/GOSs, Eu-*i*-PA-Phen/GOSs, Eu-*p*-PA-Phen/GOSs). Taking Eu-PMA-Phen/GOSs as an example, the specific synthesis steps are as follows. Firstly, 5 mL GOSs dispersions and 5 mL  $\text{EuCl}_3$  ethanol solution (0.1 mol/L) were mixed and ultrasonic for 30 minutes (noted as A solution). Secondly, 0.3812 g (1.5 mmol) of PMA and 0.1002 g (0.5 mmol) of Phen were dissolved in anhydrous ethanol (noted as B solution). Then, the B solution was slowly added within A solution, as well as strong ammonia solution was used to adjust the pH level to 6–7. After stirring for 3 h at 60°C, the obtained mixture was remained for at least 12 h at room temperature. The final products were obtained by centrifugation and washing with ethanol three times and dried for at least 8 h at 50°C. Other products (without GOSs) are obtained in the same way.

## 3. Results And Discussion

GOSs was obtained by ultrasound GO in ethanol solution. Figure 1a shows the XRD spectra of GO. A sharp peak at  $2\theta = 12.03^\circ$  which can be attributed to the (001) reflection of GO.[22] The interlayer spacing of GO is 0.735 nm which is much larger than that of pristine graphite (about 0.337 nm).[14] Fig. 1b depicts the FT-IR spectra of GO. The peaks at  $3423\text{ cm}^{-1}$ ,  $1728\text{ cm}^{-1}$ ,  $1629\text{ cm}^{-1}$ ,  $1384\text{ cm}^{-1}$ ,  $1045\text{ cm}^{-1}$  are correlated to -OH vibration, C = O stretching, C = C skeletal vibration, C-OH stretching vibration and C-O stretching vibration, respectively.[20–22] Fig. 1c shows the photographs of GOSs obtained by Metallurgical microscope. Many transparent layers have been found, which indicates that GOSs has been obtained through ultrasound.

According to our previous reports, Eu-PMA-Phen can be deposited on the surface of GOSs by  $\pi$ - $\pi$  stacking, as well as hydrogen bond interactions.[17] The composite diagram is shown in Fig. 2. Under the action of ultrasound,  $\text{Eu}^{3+}$  can enter the interlayer of GOSs and enlarges the interlayer spacing of GOSs. After complexes are formed, Eu-PMA-Phen and GOSs can interact through the  $\pi$ - $\pi$  stacking of GOSs and Phen and the hydrogen bond interactions of carboxyl groups of PMA and hydroxyl of GOSs.[23] And the colors of the obtained hybrid materials are gray and gloomy after adding GOSs. In particular, the small amount of GOSs enhances the luminescence intensity of Eu-PMA-Phen. As shown in Fig. 3, the colours of Eu-PMA-Phen and Eu-PMA-Phen/GOSs are white and gray in sunlight, respectively. And these two powders present bright red emissions unde UV light (365 nm). The luminescence intensity of Eu-PMA-Phen/GOSs is stronger than that of Eu-PMA-Phen. Their excitation and emission spectra prove this phenomenon (Fig. 4). There are a broad spectral band in the range of 200–400 nm which is attributed to f-f transitions of the ligand. The presence of GOSs enhances the intensity of f-f transitions of the ligand, which implies that GOSs enhances the energy transfer efficiency between ligand and  $\text{Eu}^{3+}$ .[24] The

emission spectra of Eu-PMA-Phen and Eu-PMA-Phen/GOSs exhibit the characteristic emission peaks of  $\text{Eu}^{3+}$ . The peaks at 580, 592, 612, 651 and 700 nm correspond to  ${}^5\text{D}_0\text{-}{}^7\text{F}_0$ ,  ${}^5\text{D}_0\text{-}{}^7\text{F}_1$ ,  ${}^5\text{D}_0\text{-}{}^7\text{F}_2$ ,  ${}^5\text{D}_0\text{-}{}^7\text{F}_3$  and  ${}^5\text{D}_0\text{-}{}^7\text{F}_4$  transitions of  $\text{Eu}^{3+}$ , respectively.<sup>25</sup> The peak at 612 nm is responsible for the red emission color, which corresponds to the red we see in Fig. 3. And the  ${}^5\text{D}_0\text{-}{}^7\text{F}_2$  transitions intensity of Eu-PMA-Phen/GOSs is stronger than that of Eu-PMA-Phen. This is why we see that Eu-PMA-Phen/GOSs is brighter than Eu-PMA-Phen. And this also shows that the presence of GOSs can improve the emission of Eu-PMA-Phen.

At present, some graphene oxide/rare-earth complex hybrid luminescent materials have been synthesized via  $\pi$ - $\pi$  stacking of GOSs and Phen. The first ligands of these materials are dibenzoylmethane,[13] 2-thenoyltrifluoroacetone,[16, 18] acetylacetone,[14] 1-(2-Naphthoyl)-3,3,3-trifluoroacetone and PMA,[15, 17] respectively. Although the existence of GOSs improves the luminescent properties of these materials, it also causes different degrees of fluorescence quenching of the obtained hybrid luminescent materials (except PMA). The quenching effect of GOSs is mainly due to its unique  $\text{sp}^2$  domain which can absorb ligand energy. But, the existence of PMA causes different phenomena. It is very important to study the special role of PMA in hybrid materials, which is helpful to design high performance graphene oxide rare earth luminescent materials. At present, it has been reported that graphene is a complete quenching agent, which can absorb the energy of many luminescent materials, according to theoretical simulation.[12, 26] The corresponding conclusions are also applicable to many graphene oxide hybrid luminescent materials.[27–28] However, there are different results in the GOSs/rare earth hybrid luminescent materials, especially PMA as the ligand. Is this particular phenomena due to the special structure of PMA? PMA is an aromatic carboxylic acid with ortho, meta and para effects. Does this special structure have a certain synergistic effect with GOSs? In recent reports, Yan et al find the structure of PA, *i*-PA and *p*-PA has different effects on room temperature phosphorescence of the obtained material.[29–30] Therefore, we split the structure of PMA and choose PA, *i*-PA and *p*-PA to represent the o-position, meta-position and para-position effect of PMA, respectively. Then, their hybrid materials are synthesized by the same method. Figure 5 shows their excitation and emission spectra. These materials have a wide absorption at 200–400 nm which is attributed to f-f transitions of the ligand, and all have characteristic emission of  $\text{Eu}^{3+}$ . [17] By comparison, we can find that the existence of the small amount of GOSs can quench the luminescence of Eu-PA-Phen obviously, greatly improve the luminescence of Eu-*i*-PA-Phen, and not completely quench the luminescence of Eu-*p*-PA-Phen. These phenomena indicate that different carboxylic acid sites with GOSs have different effects on luminescence intensity of hybrid materials. The o-position effect has no shielding effect on the quenching ability of GOSs, the energy of ligands is almost completely by GOSs. The meta-position effect can synergize with GOSs to increase the luminescence intensity of hybrid materials, the energy absorbed by GOSs is also transferred to  $\text{Eu}^{3+}$  ions. The para-position effect can shield quenching ability of GOSs, but the absorbed energy of ligands can still be absorbed by GOSs. Through the analysis of these results, it seems that the aromatic carboxylic acid ligands with meta-position structure can synergize with GOSs to improve the luminescence intensity of graphene oxide/rare earth complexes hybrid materials. However, when BTC was selected as the first ligand, the results are not consistent with the expected results. The small amount of GOSs can still reduce the luminescence intensity of hybrid materials, but it will not be completely quenched(Fig. 6). After the

structure analysis of BTC, we think that the reason for this phenomenon is: the meta-position of *i*-PA is non-uniform, while the meta-position of BTC is homogeneous, and the homogenized meta-position can not cooperate with GOSs. At the same time, when the excitation and emission spectra of Eu-PA-Phen, Eu-*i*-PA-Phen and Eu-*p*-PA-Phen are compared, we can find that the luminescence intensity of Eu-PA-Phen is the strongest (Fig. 7). This indicates that the o-position effect is most helpful for the sensitization of Eu<sup>3+</sup> ions. Combined with the above analysis, we can conclude some conclusions: the synergistic effect of PMA and *i*-PA with the small amount of GOSs can improve the luminescent intensity of the hybrid materials, which may be caused by their inhomogeneous meta-position; the aromatic carboxylic acids with o-position have the best sensitization effect on Eu<sup>3+</sup>, followed by para-position, and the worst meta-position.

As we all know that the luminescence of rare earth complexes is mainly due to the “antenna effect” between ligands and central ions, the excited triplet state of ligands is very important for their luminescent intensity.[24–25] The excited triplet states of organic ligands correspond to phosphorescent emission, so the length of phosphorescence lifetime can be used as an important index to judge the energy of excited triplet states of ligands. According to Yan et al the report, [30] the distance of  $\pi$ - $\pi$  stacking of ligands can affect their respective excited triplets and their phosphorescence lifetimes. In their report, *i*-PA with the largest  $\pi$ - $\pi$  stacking distance has the longest phosphorescence lifetime. Based on their conclusions, we can infer that the  $\pi$ - $\pi$  stacking distance between GOSs and rare earth complexes may be related to the luminescence intensity of graphene oxide/rare earth complexes. According to previous reports,[13–19] we know the energy transfer between GOSs and rare earth complexes mainly comes from  $\pi$ - $\pi$  stacking of GOSs and Phen. Therefore, the distance of  $\pi$ - $\pi$  stacking of GOS and rare earth complexes is the key factor for luminescence intensity of hybrid materials. And the quenching ability of GOSs comes from its sp<sup>2</sup> domain, the  $\pi$ - $\pi$  stacking of GOSs and Phen also makes the complexes very close to this domain causing luminescence quenching.[12, 26] However, the different first ligands can affect the distance of  $\pi$ - $\pi$  stacking between GOSs and Phen, which results in different effects of GOSs on the luminescent intensity of the complexes.

As shown in Fig. 8, the schematic diagram of the relationship between  $\pi$ - $\pi$  stacking distance and luminescence intensity of graphene oxide/rare earth complexes is assumed according to the experimental results. In this scenario, we believe that GOSs can maintain the luminescence intensity of rare earth complexes at a certain  $\pi$ - $\pi$  stacking distance  $d$ . At this distance, the energy that GOSs transfers to rare earth complexes and GOSs absorbs rare earth complexes is the same, which will not reduce the luminescence intensity of hybrid luminescent materials. When the distance between GOSs and rare earth complexes is less than the value of  $d$ , the energy absorbed by sp<sup>2</sup> domain of GOSs can increase, resulting in the luminescence quenching. When the distance is greater than  $d$  value, the ability of GOSs to absorb ligand energy will be weakened, but the energy channel between them still exists. At this time, the ability of rare earth central ions to absorb energy is still very strong. The external energy absorbed by GOSs and the photons produced by GOSs can be transferred to organic ligands together, so as to improve the sensitization of organic ligands to rare earth central ions and improve the luminescence intensity of

hybrid materials. At present, the  $d$  value can not be calculated, mainly because of the difference of the  $d$  value of different luminescent materials. And the oxygen-containing functional groups on the surface of graphene oxide and the energy level difference between organic ligands and rare earth ions in rare earth complexes also can affect the  $d$  value.

## 4. Conclusions

In conclusion, we have prepared Eu-PMA-Phen/GOSs hybrid luminescent materials, and analyzed the effect of the carboxylic acid structure of PMA on the luminescent intensity of hybrid materials. By splitting the structure of PMA, PA, *i*-PA and *p*-PA are chosen to represent the o-position, meta-position and para-position effect of PMA. The experimental results show that the o-position effect of PMA is helpful to sensitize the central Eu<sup>3+</sup> ions, the meta-position effect of PMA can cooperate with GOSs to improve the luminescence intensity of hybrid materials, and the para-position effect of PMA can weaken the quenching ability of GOSs. We believe that this work is of positive significance in the design of novel and high performance graphene oxide/rare earth aromatic carboxylic acid hybrid luminescent materials.

## Declarations

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by Department of Education of Hebei Province (No. ZD2017214).

## References

- [1] W. Choi, I. Lahiri, R. Seelaboyina, Y. S. Kang, *Critical Reviews in Solid State and Materials Sciences* 35 (2010) 52-71.
- [2] Y. Shao, J. Wang, H. Wu, J. Liu, I. A. Aksay, Y. Lin, *Electroanalysis* 22 (2010) 1027-1036.
- [3] K. P. Loh, Q. Bao, G. Eda, M. Chhowalla, *Nature Chemistry* 2 (2010) 1015.
- [4] K. Yang, L. Feng, X. Shi, Z. Liu, *Chemical Society Reviews*, 42 (2013) 530-547.
- [5] Z. Yin, J. Zhu, Q. He, X. Cao, C. Tan, H. Chen, Q. Yan, H. Zhang, *Advanced Energy Materials* 4 (2014) 1300574.
- [6] R.S. Edwards, K.S. Coleman, *Nanoscale* 5 (2013) 38-51.

- [7] J. Chen, Y. Li, L. Huang, C. Li, G. Shi, Carbon 81 (2015) 826-834.
- [8] Y. Zhu, S. Murali, W. Cai, X. Li, J.W. Suk, J.R. Potts, R.S. Ruoff, Advanced Materials 22 (2010) 3906-3924.
- [9] M. A. Rafiee, J. Rafiee, Z. Wang, H. Song, Z. Yu, N. Koratkar, ACS Nano 3 (2009) 3884-3890.
- [10] Q. Wu, Y. Xu, Z. Yao, A. Liu, G. Shi, ACS Nano 4 (2010) 1963-1970.
- [11] J. Liu, H. Bai, Y. Wang, Z. Liu, X. Zhang, D.D. Sun, Advanced Functional Materials 20 (2010) 4175-4181.
- [12] J. Kim, L. J. Cote, F. Kim, J. Huang, Journal of the American Chemical Society 132 (2009) 260-267.
- [13] Y. Cao, T. Yang, J. Feng, P. Wu, Carbon 49 (2011) 1502-1504.
- [14] S. Wang, J. Hu, Y. Wang, F. Luo, Journal of Materials Science 48 (2013) 805-811.
- [15] C. Zhao, L. Feng, B. Xu, J. Ren, X. Qu, Chemistry–A European Journal 17 (2011) 7007-7012.
- [16] X. Fan, K. Shang, B. Sun, L. Chen, S. Ai, Journal of Materials Science 49 (2014) 2672-2679.
- [17] W. Zhang, X. Zou, J. Zhao, Journal of Materials Chemistry C 3 (2015) 1294-1300.
- [18] Y. Zhao, L. Huang, Y. Wang, J. Tang, Y. Wang, J. Liu, L.A. Belfiore, M.J. Kipper, Journal of Alloys and Compounds 687 (2016) 95-103.
- [19] Y. Li, S. Qiu, T. Du, W. Wei, Z. Han, F. Ruan, L. Cao, Chinese Journal of Inorganic Chemistry 35 (2019) 174-182.
- [20] W. Zhang, X. Zou, J. Zhao, Journal of Materials Chemistry C 3 (2015) 2788-2791.
- [21] W. Zhang, X. Zou, H. Li, J. Hou, J. Zhao, J. Lan, B. Feng, S. Liu, RSC Advances 5 (2015) 146-152.
- [22] X. Zou, W. Zhang, RSC Advances 5 (2015) 55143-55149.
- [23] X. Zhang, W. Zhang, Y. Li, C. Li, Dyes and Pigments 140 (2017) 150-156.
- [24] P. Li, Y. Wang, H. Li, G. Calzaferri, Angewandte Chemie International Edition 53 (2014) 2904-2909.
- [25] D. Yang, Y. Wang, Z. Li, Y. Xu, F. Cheng, P. Li, H. Li, Journal of Materials Chemistry C 6 (2018) 1153-1159.
- [26] L. Xie, X. Ling, Y. Fang, J. Zhang, Z. Liu, Journal of the American Chemical Society 131 (2009) 9890-9891.
- [27] D. Xu, X. Li, J. Liu, L. Huang, Journal of Rare Earths 31 (2013) 1085-1091.

[28] D. R. Dreyer, S. Murali, Y. Zhu, R. S. Ruoff, C. W. Bielawski, *Journal of Materials Chemistry C* 21 (2011) 3443-3447.

[29] R. Gao, D. Yan, *Chemical Science* 8 (2017) 590-599.

[30] B. Zhou, D. Yan, *Advanced Functional Materials* 29 (2019) 1807599.

## Figures

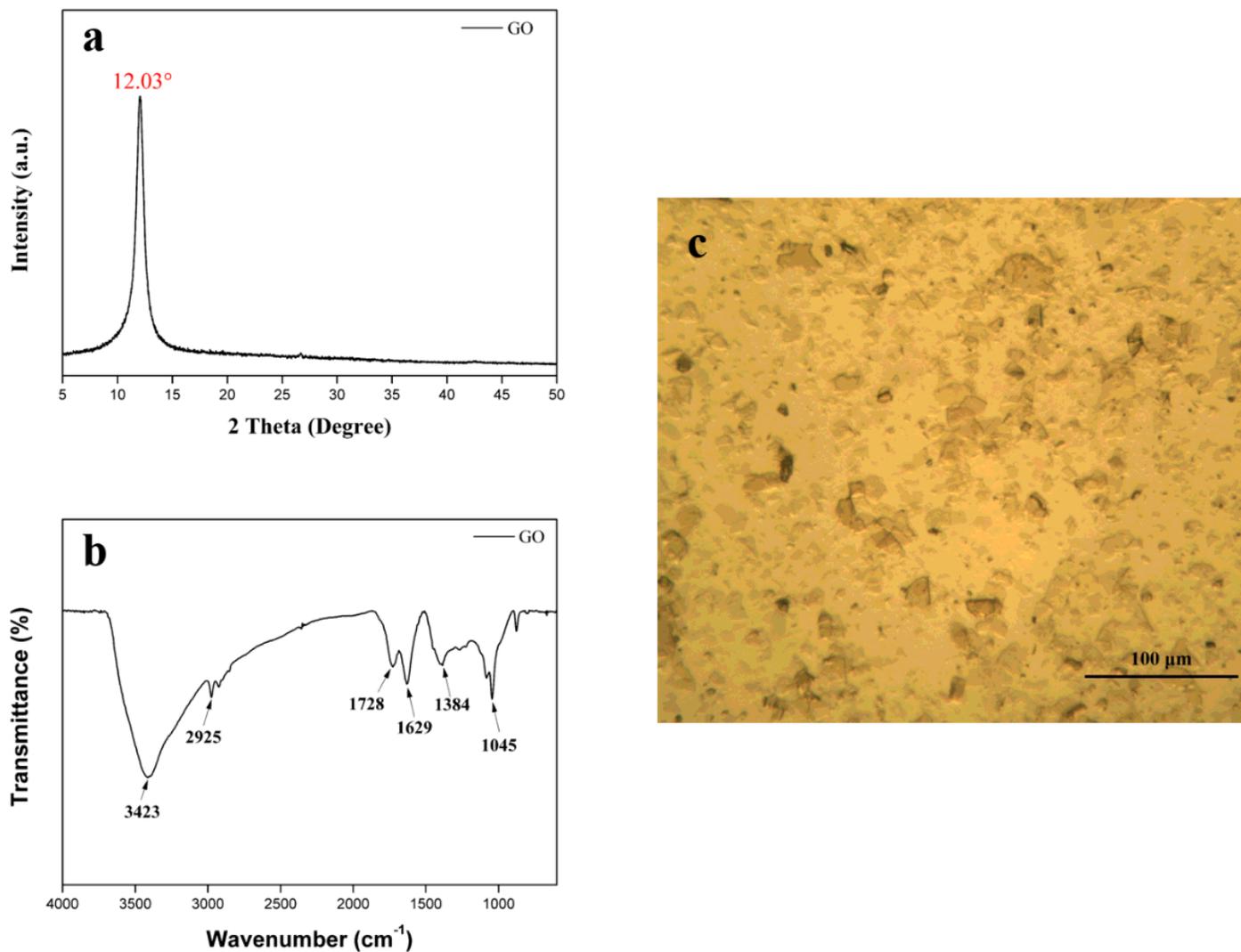
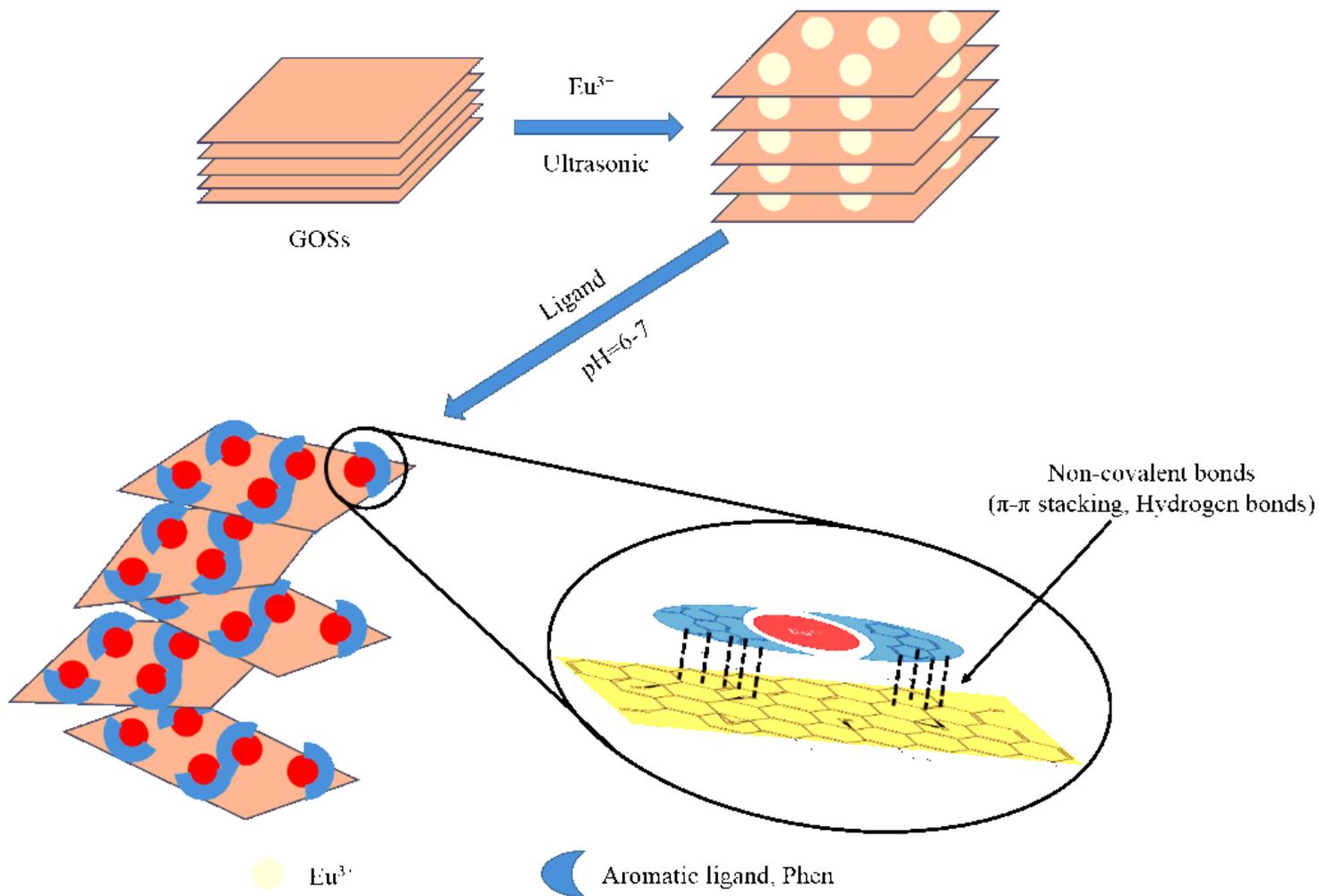


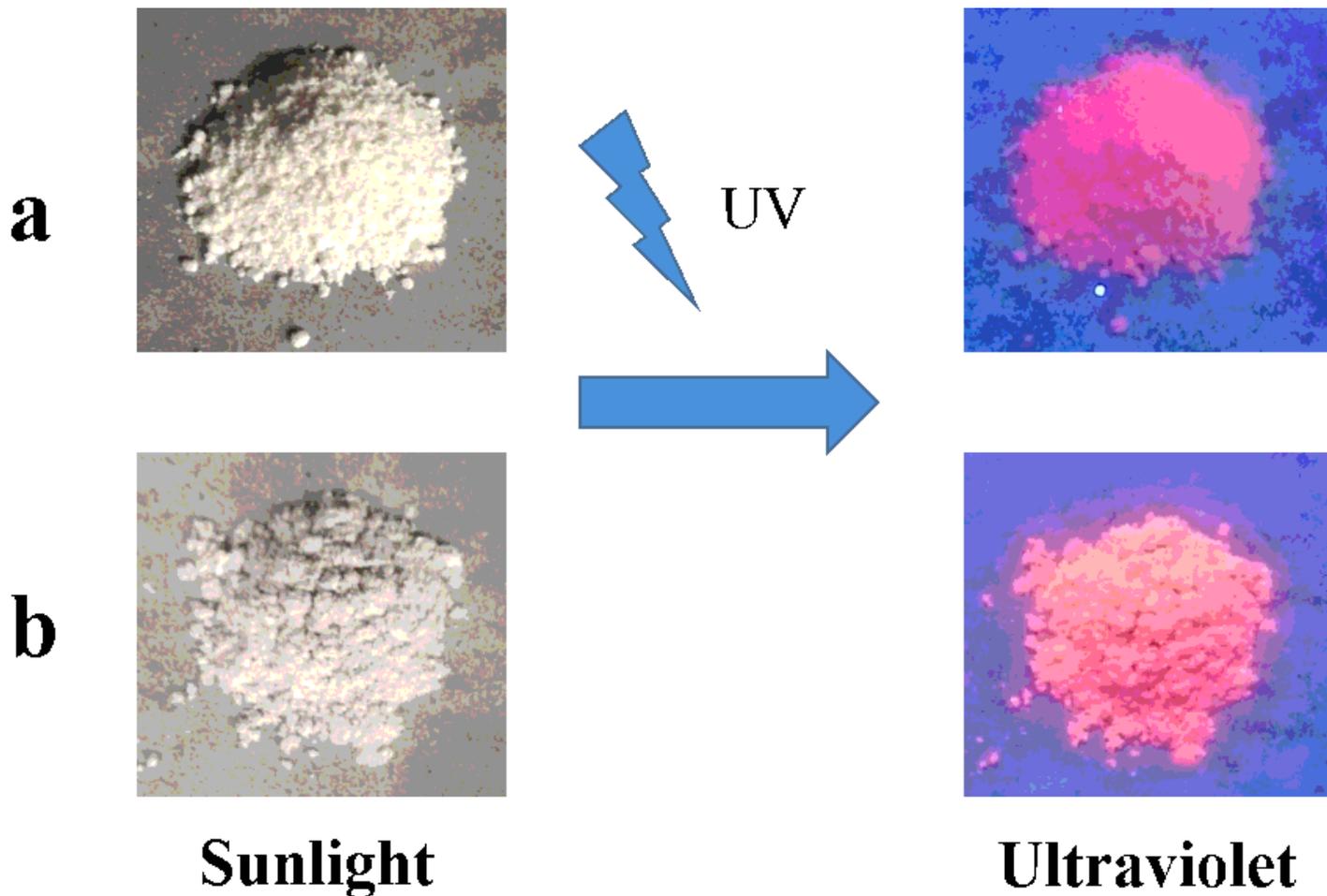
Figure 1

(a) the XRD spectra of GO, (b) the FT-IR spectra of GO, (c) the photographs of GOSs.



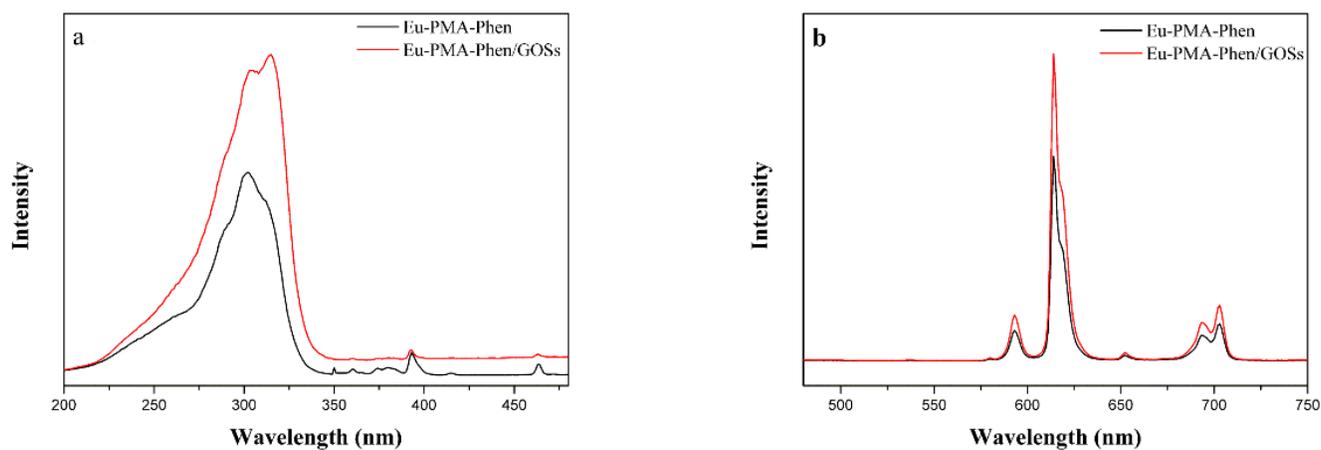
**Figure 2**

The composite diagram of Eu-PMA-Phen/GOSs.



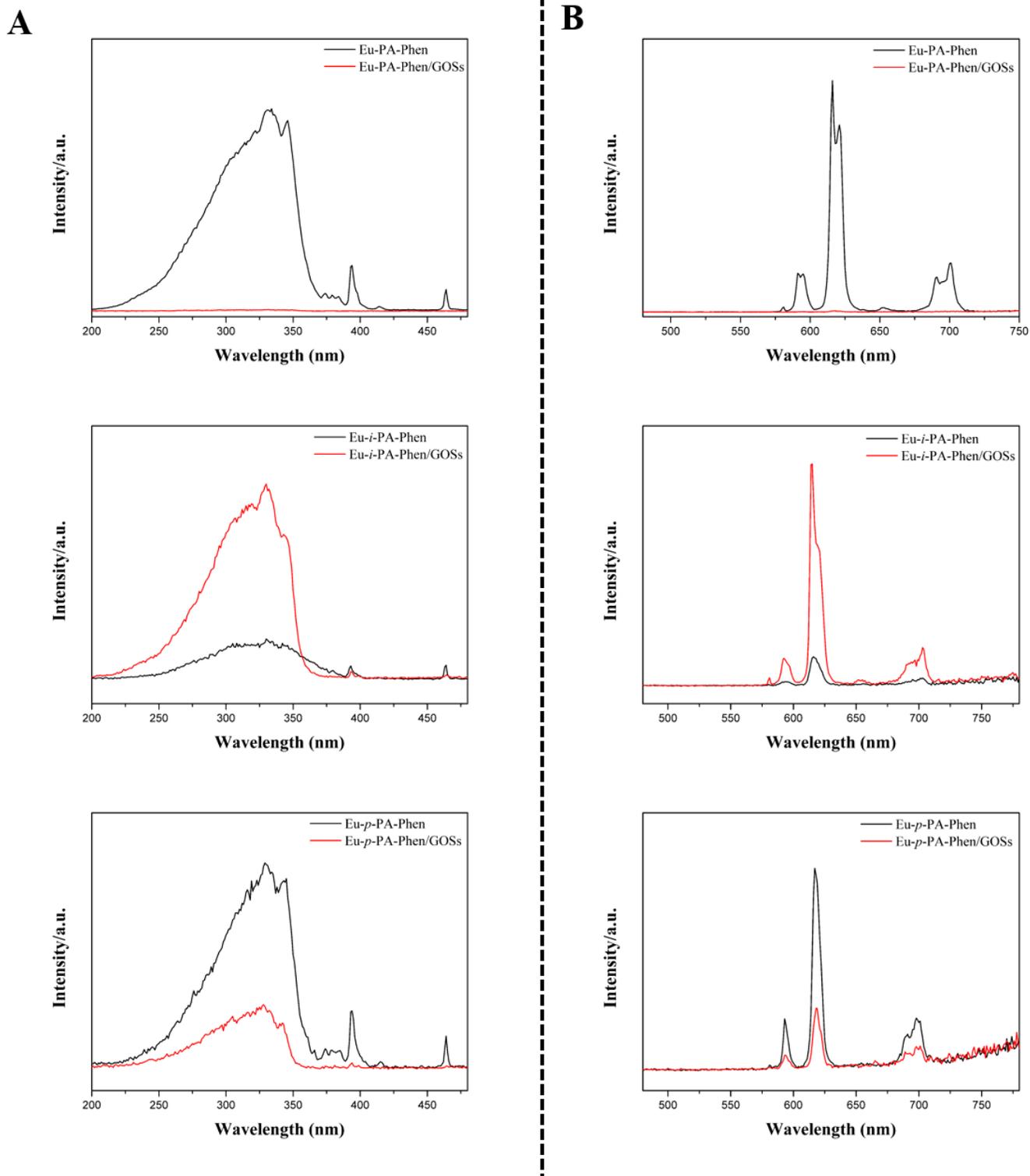
**Figure 3**

The digital images of Eu-PMA-Phen (a) and Eu-PMA-Phen/GOSs (b).



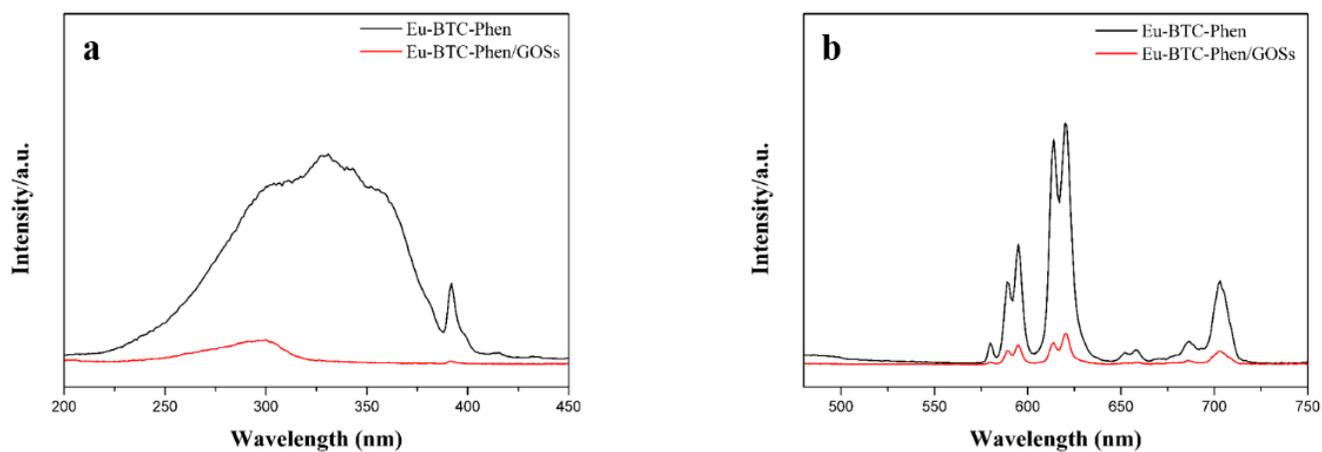
**Figure 4**

The excitation spectra (a) and emission spectra (b) of Eu-PMA-Phen and Eu-PMA-Phen/GOSs.



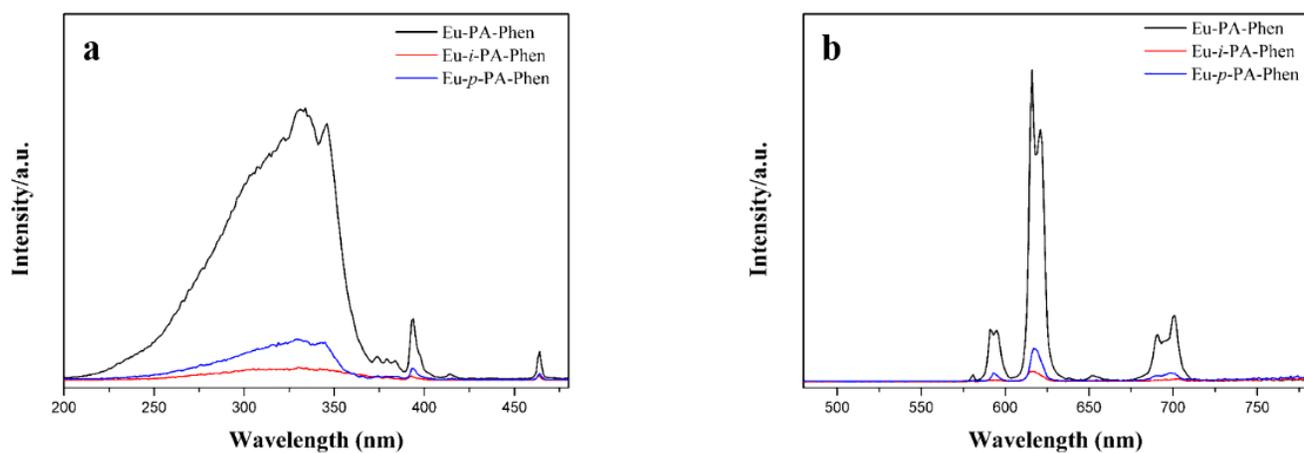
**Figure 5**

The excitation (A) and emission spectra (B) of Eu-PA-Phen, Eu-PA-Phen/GOSs, Eu-*i*-PA-Phen, Eu-*i*-PA-Phen/GOSs, Eu-*p*-PA-Phen and Eu-*p*-PA-Phen/GOSs.



**Figure 6**

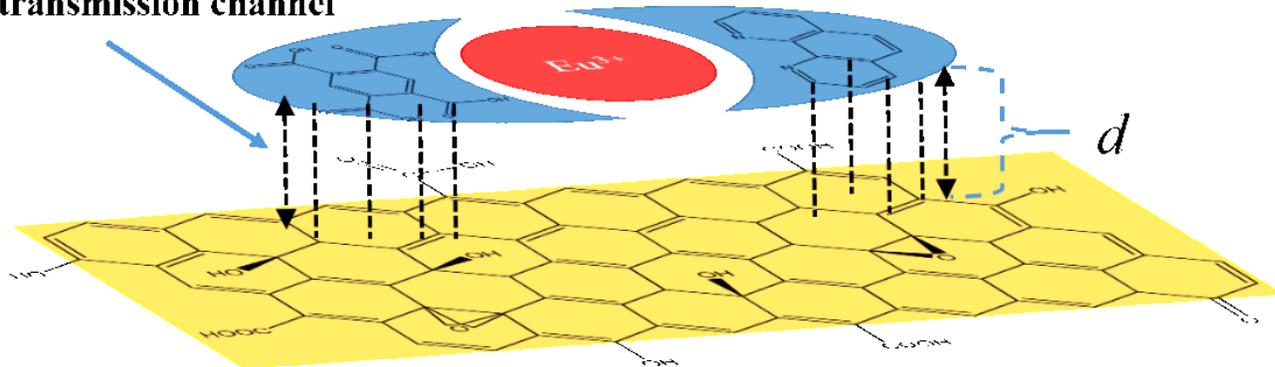
The excitation (a) and emission spectra (b) of Eu-BTC-Phen, , Eu-BTC-Phen/GOSs.



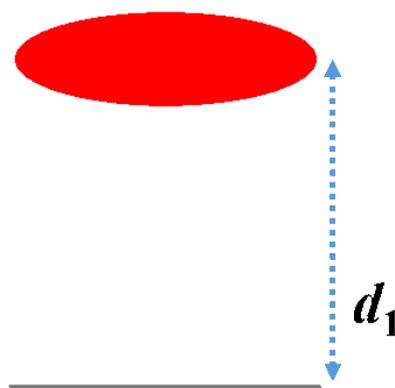
**Figure 7**

The excitation (a) and emission spectra (b) of Eu-PA-Phen, , Eu-i-PA-Phen and Eu-p-PA-Phen.

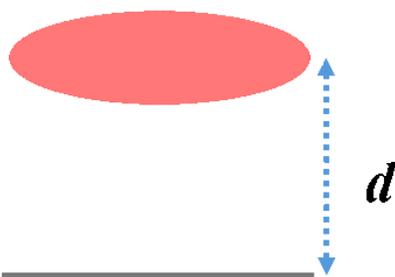
### Energy transmission channel



### Luminescence enhancement



### Luminescence quenching



$$d_2 < d < d_1$$

———— GOSs     Rare earth complexes

Figure 8

The simplified schematic diagrams showing the influence of the  $\pi$ - $\pi$  stacking distance of GOSs and rare earth complexes on luminescence intensity.