新型β-二酮稀土配位聚合物杂化发光材料的合成和应用

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引言

β-二酮稀土配合物具有独特的发光机制及一系列优良的发光性能，因而被广泛地应用在分析化学、生命科学、光学器件等领域。[1]小分子稀土配合物的光、热和化学稳定性差，限制了其在很多领域的应用。本研究设计合成了一类新型β-二酮聚合物，通过化学键作用将稀土离子（Eu^{3+}, Gd^{3+}）配合到聚合物中，自组装制备新型稀土发光材料，用于金属离子与气体荧光传感器和多模态生物细胞成像等领域。研究表明，所合成的β-二酮均聚铕复合物荧光传感器稳定性良好，能可视化检测痕量金属离子，并对酸碱性气体快速荧光响应、可多次循环利用。[2] 螯合Eu^{3+}和Gd^{3+}双稀土离子的β-二酮嵌段聚合物可自组装形成胶束并实现MRI和荧光双模态成像，其生物相容性好，成像效果明显。[3]

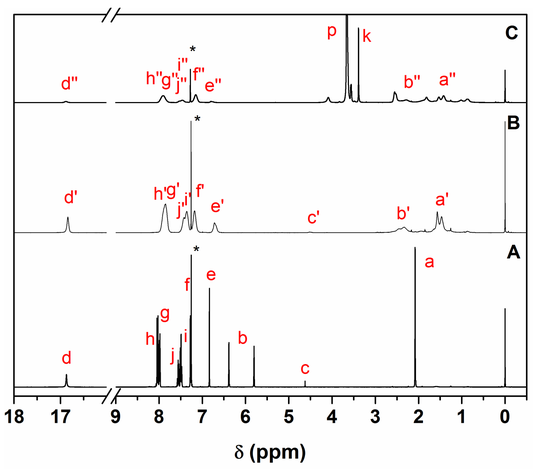
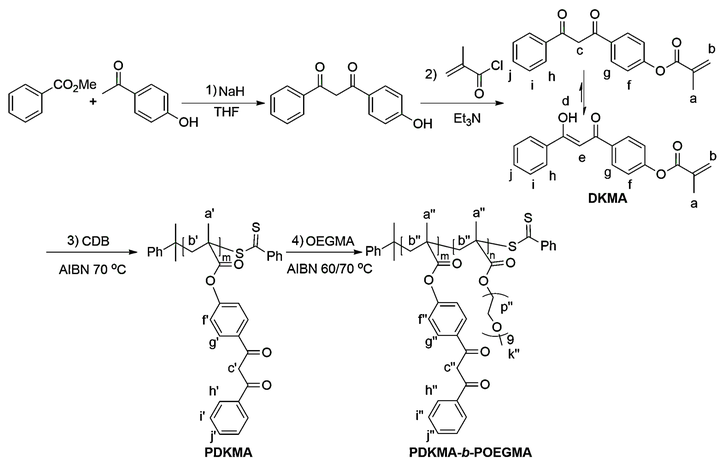


Fig. 1 ^{1}H NMR spectra of DKMA (A), PDKMA (B) and PDKMA-*b*-POEGMA (C) with the assignments in **Scheme 1**, *: residue $CHCl_3$ in solvent $CDCl_3$.



Scheme 1. Synthetic route for homo-polymer PDKMA and diblock copolymer PDKMA-*b*-POEGMA via sequential RAFT protocol

Table 1. RAFT homo- and block co-polymerization of DKMA with OEGMA.

Sample	Polymers	[M]/[CTA]/[I][a]	Time (h)	Temp. (℃)	Con. (%)	$M_{n,thero}$ (kDa)[b]	$M_{n,SEC}$ (kDa)[c]	$Đ$[b]
PD1	$PDKMA_{152}$[d]	900/3/1	10.5	70	56	47.1	33.8	1.28
PD2	$PDKMA_{69}$[d]	300/3/1	10.0	70	69.3	21.5	16.3	1.30
PD3	$PDKMA_{50}$[d]	300/3/1	7.5	70	49.5	15.7	12.8	1.30
PDO1	$PDKMA_{152}$-b-$POEGMA_{310}$[e]	900/3/1	3.7	70	77.4	202.1	79.8	1.33
PDO2	$PDKMA_{69}$-b-$POEGMA_{43}$[e]	375/3/1	11.2	60	29	43.0	20.8	1.33
PDO3	$PDKMA_{50}$-b-$POEGMA_{50}$[e]	300/3/1	6.0	60	30	40.7	18.2	1.36

a) Molar ratio of monomer (M), CTA (CDB or PDKMAs) and AIBN (I) in feed. b) Trioxymethylene was taken as an initial sample to monitor the conversion by ^{1}H-NMR spectroscopy, and DP was measured by comparing the experimental conversion with desired conversion. c) $M_{n,\,calc} = M_{monomer} \times ([M]/[CTA]) \times Conversion + M_{CTA}$. d) Determined from SEC in THF calibrated by PS standards. e) M_n was determined by MALLS. f) PDKMA-*b*-POEGMAs composition determined by ^{1}H NMR according to [DKMA]/[OEGMEMA] = I(Ar*H*)/I(OCH_2CH_2O).

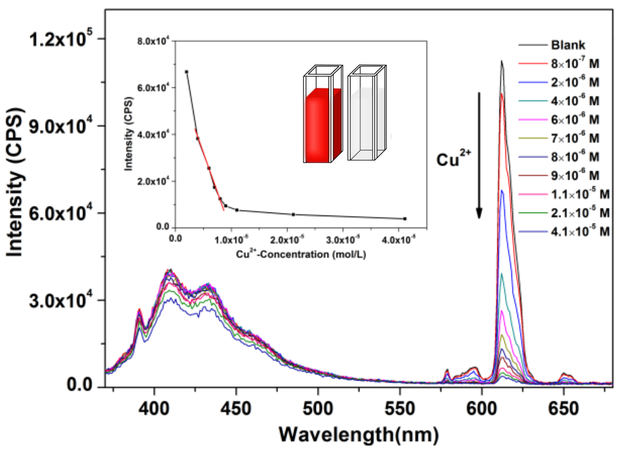


Fig. 2. Luminescence spectra of Eu^{3+}-$PDKMA_{67}$ in THF/water solution with different Cu^{2+} concentrations under excitation at 350 nm at 25 ° C. Inset: the photoluminescence intensity tendency at 612 nm as a function of various Cu^{2+} concentrations.

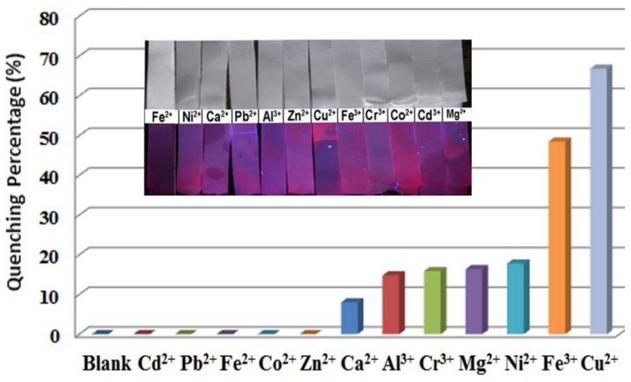


Fig. 3. Photoluminescence quenching intensity of the $^5D_0 \rightarrow {}^7F_2$ transition (612 nm) as a function of various cationic species in aqueous solution. Insets: photographs of PEP-strips with different cations under sunlight (top) and UV light of 365 nm (bottom).

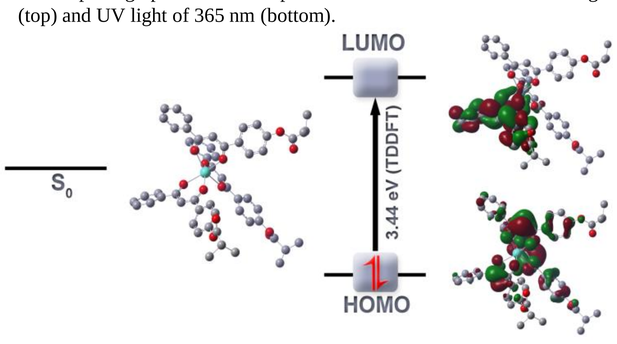


Fig. 4.. Optimized geometries of chelation of Eu^{3+} with three DKMA repeating units and the frontier molecular orbitals.

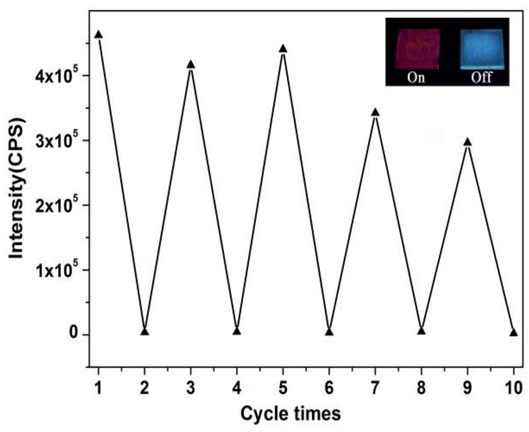


Fig 5. Responses of luminescence intensities at 612 nm of Eu^{3+}-PDKMA film coated quartz substrate (excitation: 350 nm) during several alternate acid and base vapors exposure cycles. Inset: photo of the Eu^{3+}-$PDKMA_{67}$ film upon short exposure with NH_3 (On) and HCl (Off).

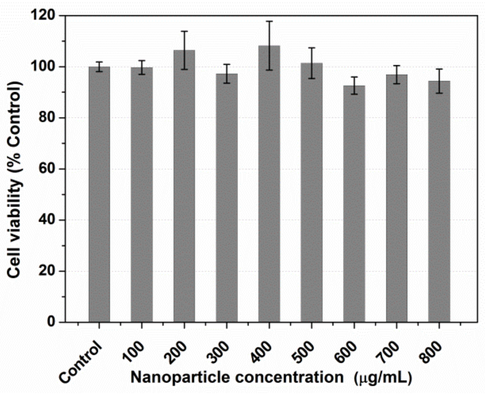


Fig. 7. Relative cell viability of NPDO1 for MCF-7 cells after 48 h incubation at a concentration between 0 to 800 μg/mL.

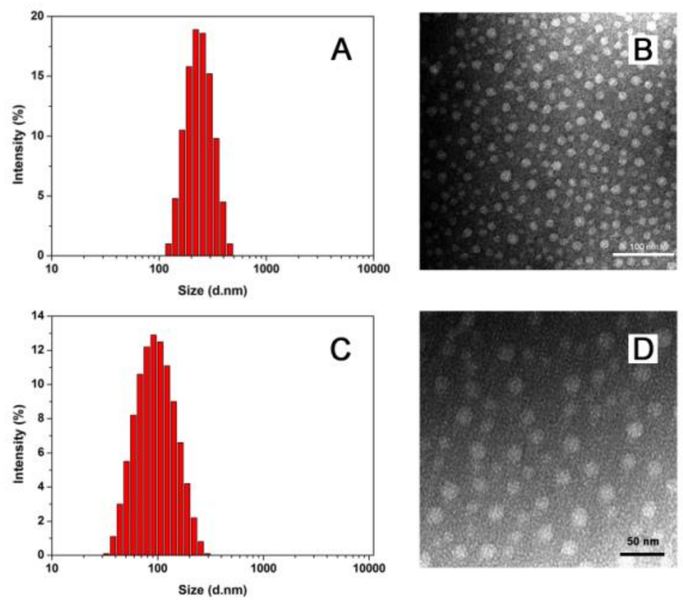


Fig 6. Size distributions histograms (A and C) and TEM images (B and D) of NPDO1 (A and B) and NPDO3 (C and D) nanoparticles in aqueous media at 25 ° C. The scale bars in B and D are 100 and 50 nm, respectively.

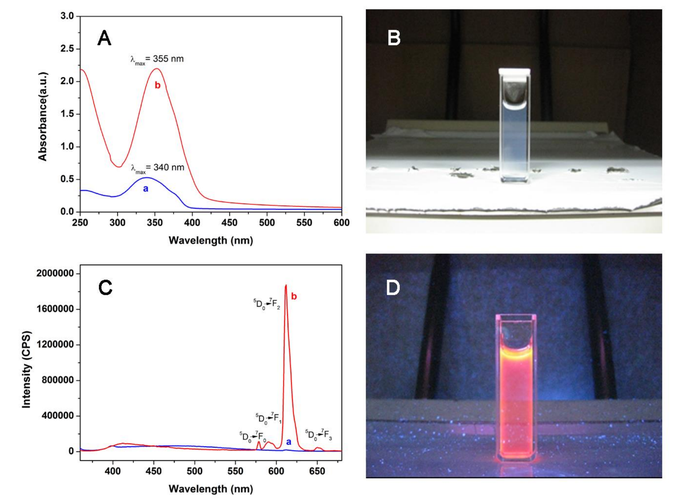


Fig. 8. (A):UV-vis of 0.04 mg/mL PDO1(a) and 0.073 mg/mL PDO1 with Ln^{3+}(b) in aqueous media, (B): Photographs of solution NPDO1 under sunlight, (C): PL spectra of a (PDO1, 0.0004 mg/mL mg/mL) and b (NPDO1, 0.00066 mg/mL) in aqueous media under excitation at 350 nm at 25 ºC, (D) Photographs of solution NPDO1 under UV lamp at 365 nm.

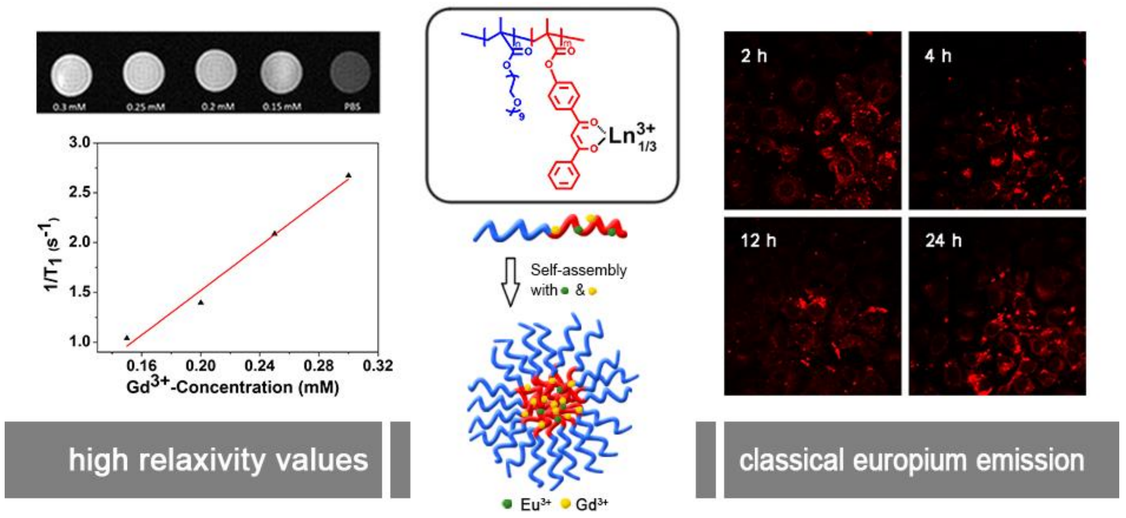


Fig. 9. Plots of longitudinal ($1/T_1$) for aqueous solutions of Gd^{3+}-chelated polymer micelle (NPDO1) at various concentrations, inset: T_1-weighted spin-echo MR images recorded in versus Gd^{3+}-concentrations of NPDO1 and PBS was measured as references. CLSM images of MCF-7 cells incubated with NPDO1 for 2~24 h at 37 ºC.

结论

- 制备了一种新型β-二酮功能聚合物(PDKMA)荧光化学传感器用于特异性高灵敏度检测铜离子和酸碱气体。在特定范围内，PDKMA对铜离子的响应呈线性关系，所制备的传感器样条响应速度快，稳定性好并可多次循环使用。
- 含β-二酮功能片段的两亲性嵌段聚合物(PDKMA-*b*-POEMGA)一步法同时螯合Eu^{3+}和Gd^{3+}离子自组装形成胶束，简便地构建了MRI/荧光成像双模态纳米探针，其生物相容性好，成像效果明显，为新型稀土配合物发光材料的设计和合成提供了新思路。

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参考文献：

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3）Fangyi Cao, Tongcun Huang, Yifei Wang, Fei Liu, Lumin Chen, Jun Ling, Jihong Sun, *Polymer Chemistry*, **2015**, 7949-7957.