Electronic Supplementary Material (ESI) for RSC Advances

White Photoluminescent Material Based on a Functional Polysiloxane Complex with Lanthanide Ions (Eu^{3+} and Dy^{3+})

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Supporting Information

1. Materials

Synthesis of α, ω-hydride terminated polydimethylsiloxane (HP).

Synthesis of N, N'-diphenyl-2-allylmalonamide (MA).

Synthesis of α, ω-N, N'-diphenylmalonamide terminated polydimethylsiloxane (PMP).

2. References

Caption of Figures

Supporting Information

1. Materials:

All the basic reagents and solvents were purchased from the Chinese National Medicine Group. Octamethylcyclotetrasiloxane (D_4) and tetramethyldisiloxane (M^HM^H) were purified by distillation before use. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone before use. Diethyl malonate and aniline were used without further purification. Platinumcyclovinylmethylsiloxane catalyst (Pt catalyst) was synthesized according to the literature[1]. Rare earth nitrates ($Ln(NO_3)_3 \cdot 6H_2O$, Ln=Eu and Dy) were obtained from the corresponding oxides in dilute nitric acid[2, 3].

1.1 Synthesis of α, ω-hydride terminated polydimethylsiloxane (HP). A mixture of D_4 and M^HM^H was heated to 65 °C and kept stirring for 10 h in nitrogen, catalyzed by 5 %wt activated clay. The activated clay was removed by filtration when the reaction was complete. The substances with boiling points lower than 100 °C under 1.3 kPa were evaporated away. Then HP was obtained as colorless liquid. ^{1}H NMR (300 MHz $CDCl_3$): δ 4.81 (s, 1H，$O–Si(CH_3)_2–\mathbf{H}$), 0.31 (d, J = 2.76 Hz, 6H, $O–Si(C\mathbf{H}_3)_2–H$), 0.21 (t, J = 2.98, 2.98 Hz, 30H, $O–Si(C\mathbf{H}_3)_2–O$) (Figure S1). ^{31}Si NMR (300MHz, $CDCl_3$): δ -6.96, -19.92, -21.92 (Figure S2). $\overline{M}_n$ =874 g·mol^{-1} (calculated from ^{1}H NMR data).

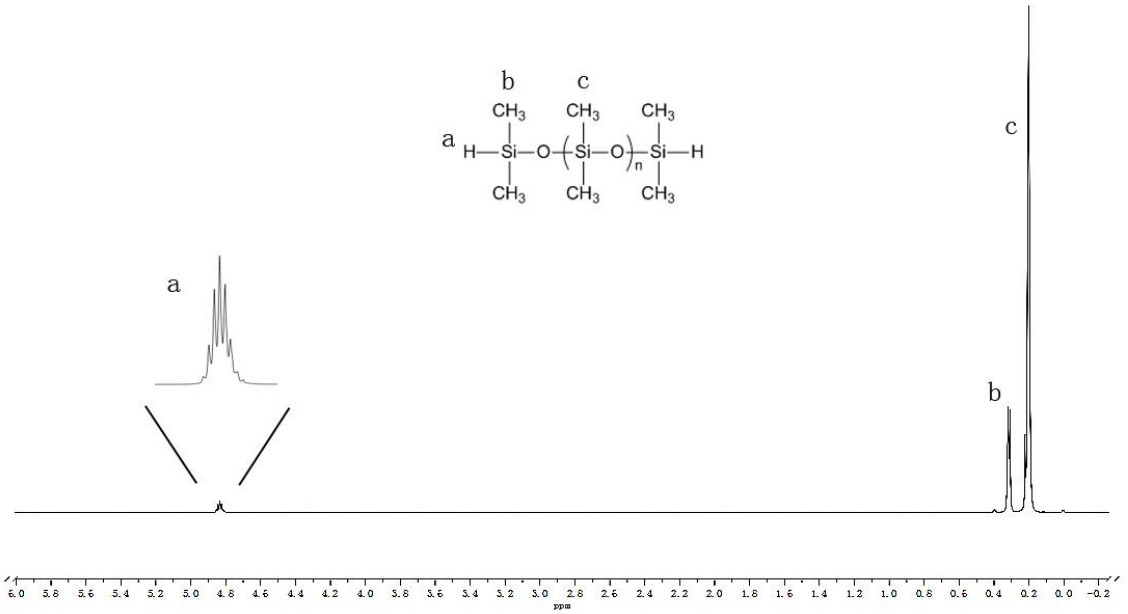

Figure S1 ^{1}H NMR spectrum of HP

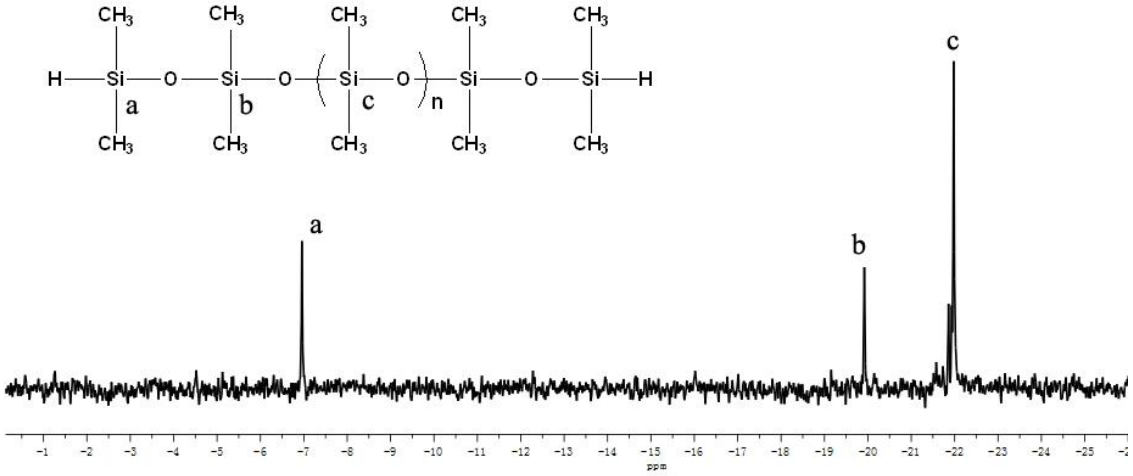

Figure S2 ^{31}Si NMR spectrum of HP

1.2 Synthesis of N, N'-diphenyl-2-allylmalonamide (MA). Diethyl malonate was added into a flask with three times excessive aniline. 50 mL of xylol was used as solvent. The mixture was kept refluxing at 120 °C for 5 h. Ethanol was distilled out of the system as soon as it was produced during the reaction. Then the mixture was cooled down to room temperature. MA precipitated from the solution was obtained as white powder by filtration. Yield: 72%. ^{1}H NMR (300 MHz, DMSO): δ 9.96 (m, 2H, a), 7.60

(dd, J = 8.6, 1.0 Hz, 4H, b), 7.30 (m, 4H, c), 7.05 (m, 2H, d), 5.83 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H, e), 5.14 (dd, J = 17.2, 1.9 Hz, 1H, f), 5.03 (m, 1H, g), 3.60 (t, J = 7.4 Hz, 1H, h), 2.67 (t, J = 7.0 Hz, 2H, i) (Figure S3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 168.36, 136.81, 132.88, 128.50, 124.43, 119.92, 118.13, 55.63, 36.87 (Figure S4).

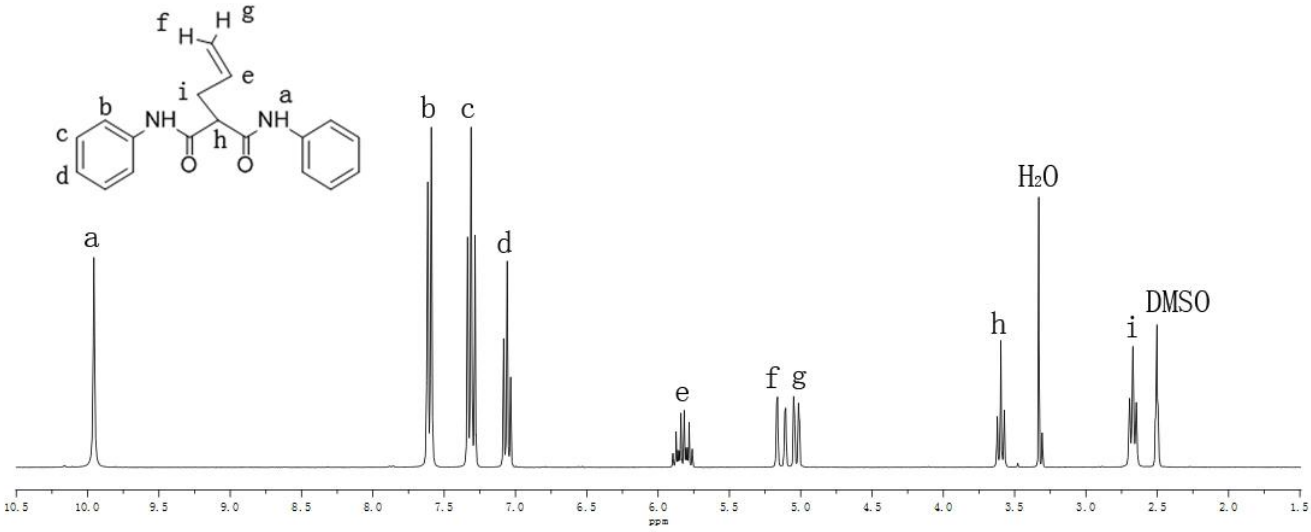

Figure S3 ^{1}H NMR spectrum of MA

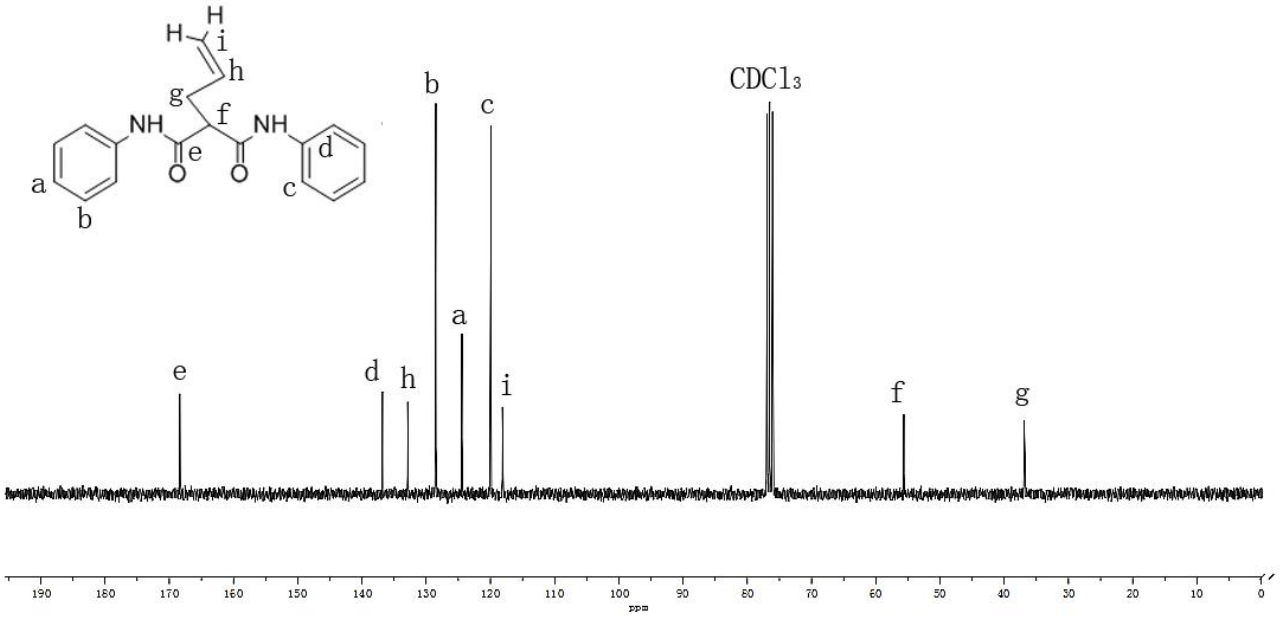

Figure S4 ^{13}C NMR spectrum of MA

1.3 Synthesis of α, ω-N, N'-diphenylmalonamide terminated polydimethylsiloxane (PMP). 10 mmol HP was mixed with 22 mmol MA in a three-necked flask in nitrogen. Then 50 mL of THF and 0.3 mL Pt catalyst were added into the mixture. The system was kept stirring at 90 °C until the FT-IR peak of the Si-H band at 2127 cm^{-1} disappeared. After evaporation of the solvent and separation of the catalyst, residual MA was separated using diethyl ether. Then brown solid PMP was obtained. The synthesis process of PMP was shown in Figure S5. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.33 (d, J = 9.3 Hz, 6H), 7.52 (m, 12H), 7.23 (t, J = 7.8 Hz, 12H), 7.04 (t, J = 7.3 Hz, 6H), 3.73 (m, 2H), 3.48 (m, 1H), 2.01 (m, 4H), 1.41 (m, 2H), 1.15 (m, 2H), 1.08 (m, 4H), 0.82 (dt, J = 23.1, 7.4 Hz, 6H), 0.49 (m, 4H), 0.00 (d, J = 2.6 Hz, 108H) (Figure S6). ^{13}C NMR (300 MHz, $CDCl_3$): δ 169.39, 137.08, 128.46, 124.33, 119.90, 55.81, 36.75, 21.01, 17.34, 13.07, 0.55 (Figure S7). ^{31}Si NMR (300 MHz, $CDCl_3$): δ 6.99, -21.27, -21.92 (Figure S8). $\overline{M}_n$ =1462 g·mol^{-1} (calculated from ^{1}H NMR data).

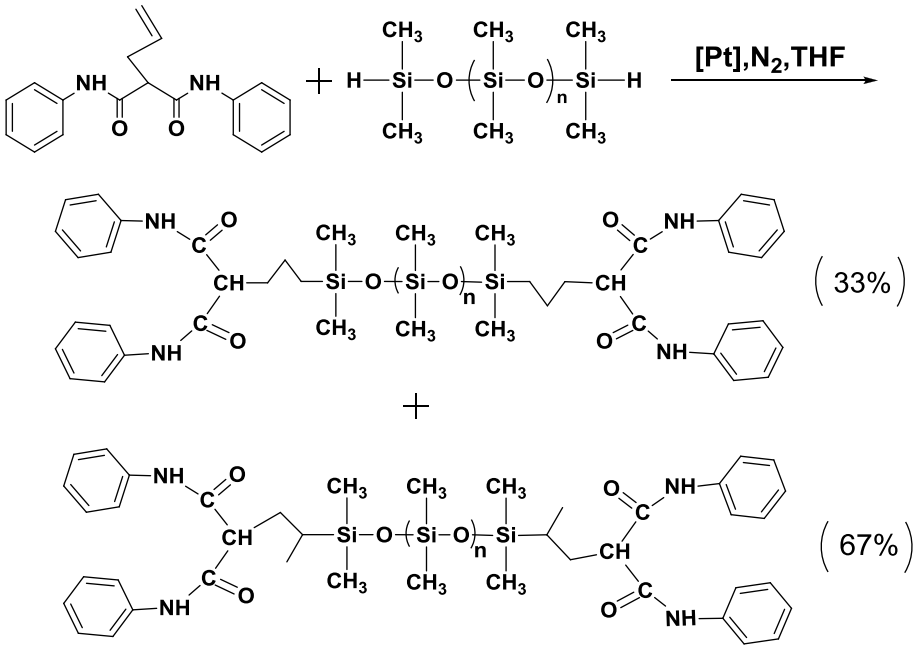

Figure S5 Synthesis of PMP

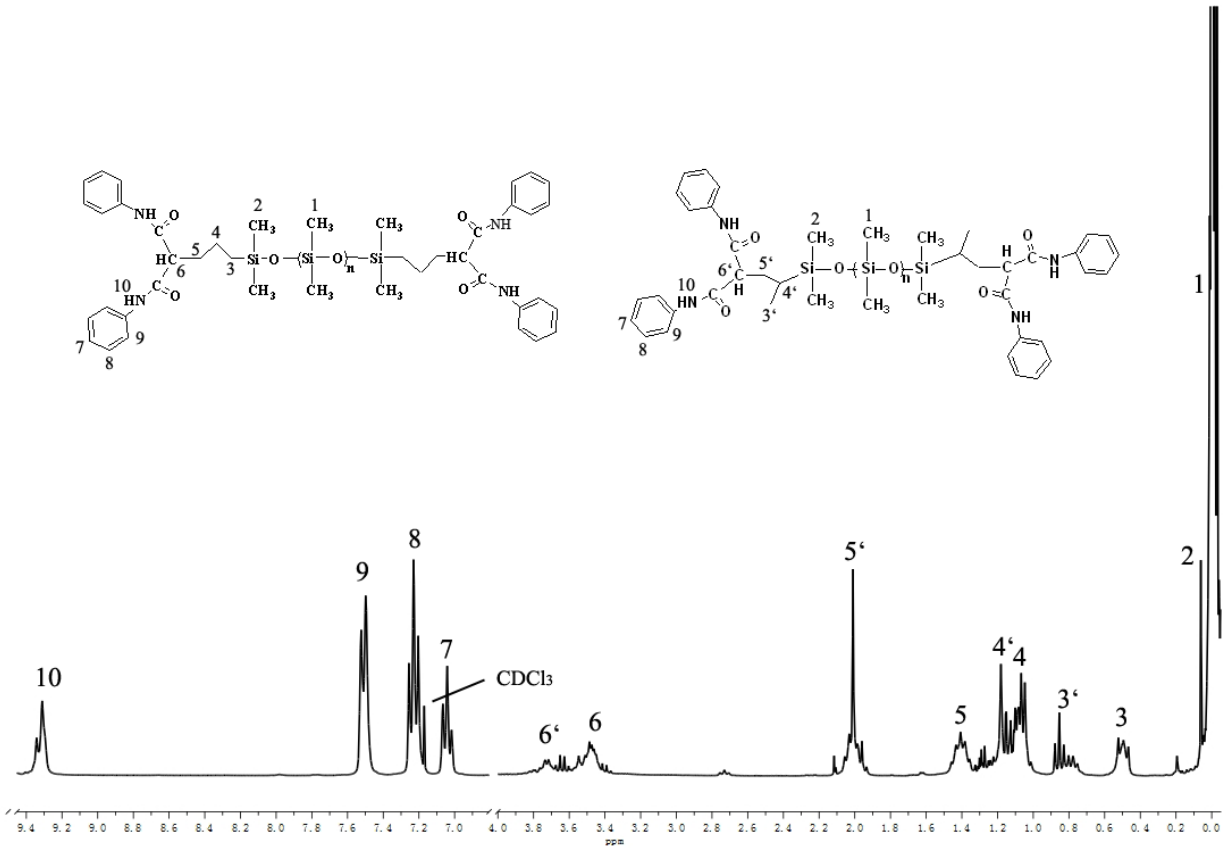

Figure S6 ^{1}H NMR spectrum of PMP

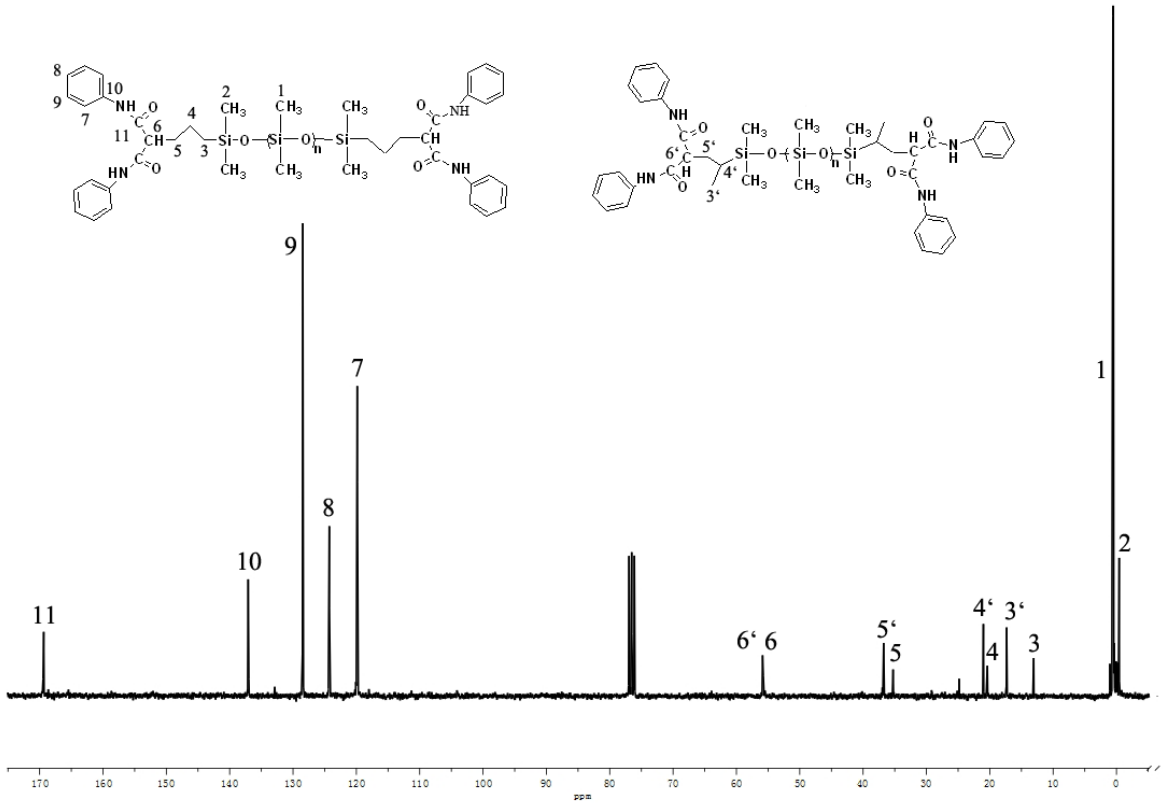

Figure S7 ^{13}C NMR spectrum of PMP

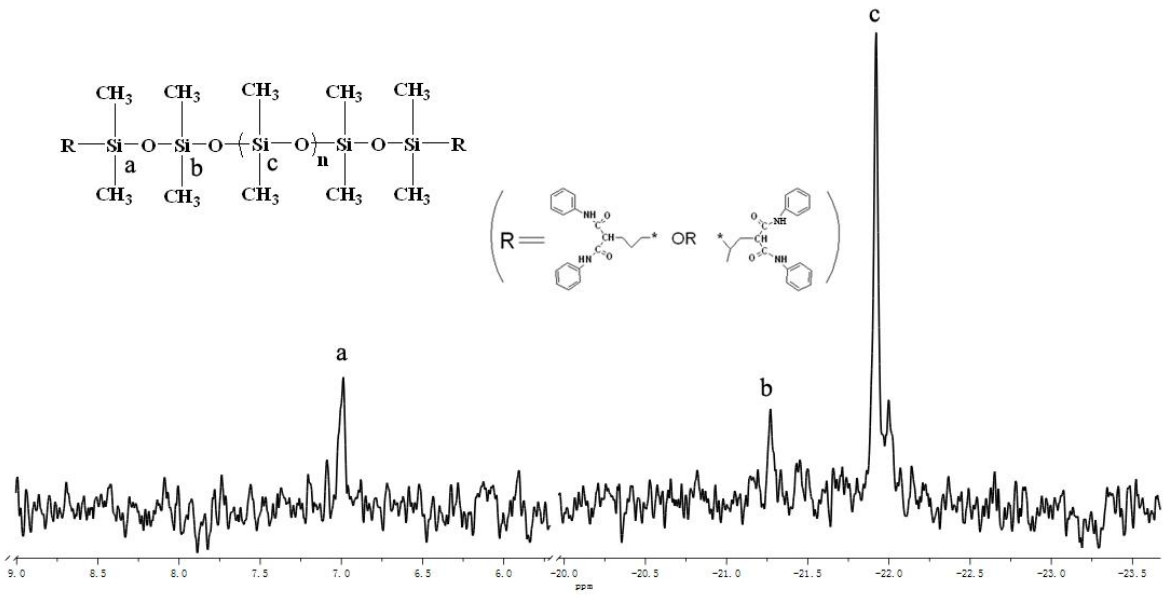

Figure S8 ^{31}Si NMR spectrum of PMP

2 References

[1] A.Ashby B. Platinum Complex Catalysts. US: General Electric Company; 1983.

[2] Liu L, Lu H, Wang H, Bei Y, Feng S. Luminescent organo-polysiloxanes containing complexed lanthanide ions. Applied Organometallic Chemistry. 2009;23:429-33.

[3] Lu H, Wang X, Wang H, Feng S. Molecular design and photophysical properties of acylamido side functionalized polysiloxanes with lanthanide ions as luminescent centers. Journal of Photochemistry and Photobiology A: Chemistry. 2010;215:48-53.