

## Supplementary Material

# Re(I) complexes as backbone substituents and cross-linking agents for hybrid luminescent polysiloxanes and silicone rubbers

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## NMR spectra of Cl-CMSs, Cl-PDMS, and N<sub>3</sub>-PDMS

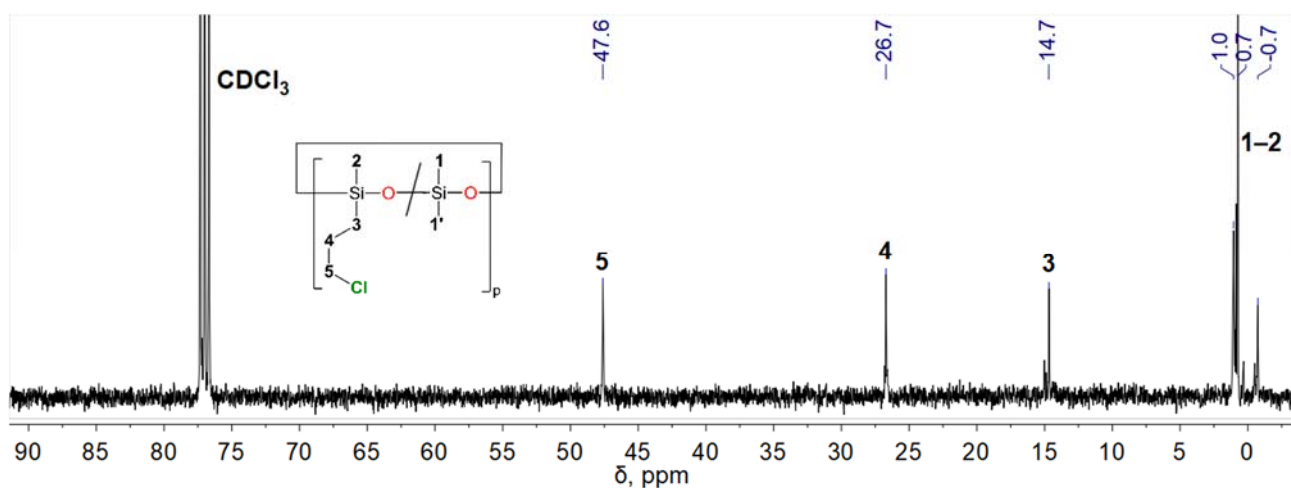


Figure S1. <sup>13</sup>C NMR spectrum of Cl-CMSs.

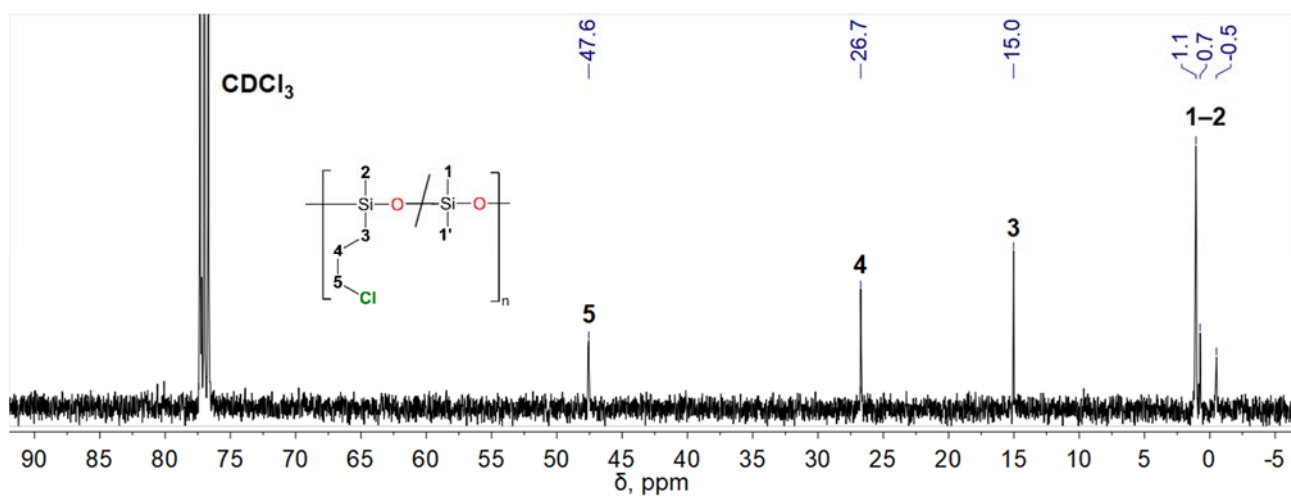


Figure S2. <sup>13</sup>C NMR spectrum of Cl-PDMS.

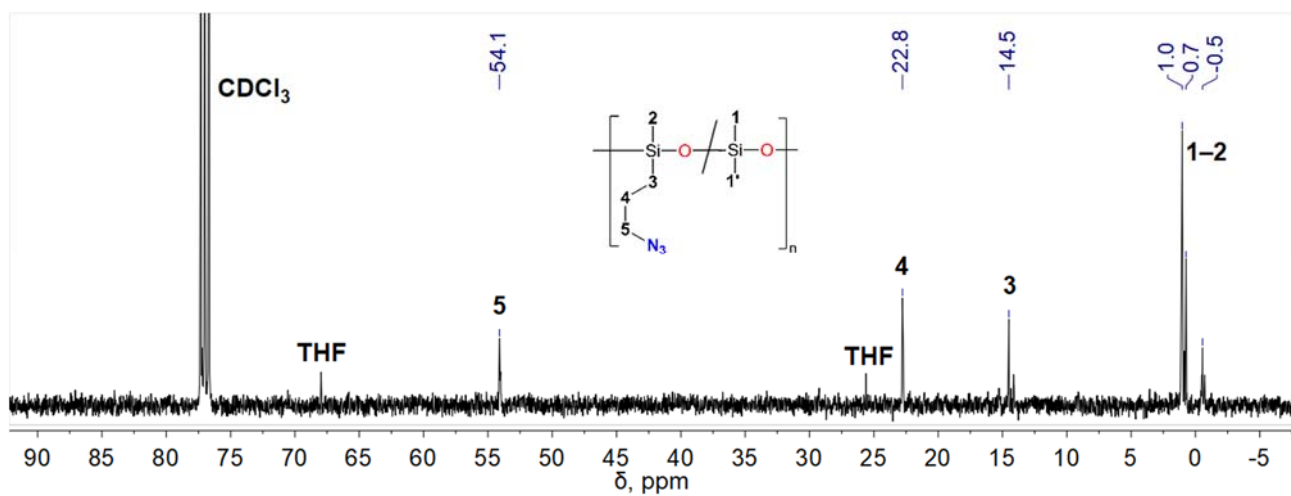
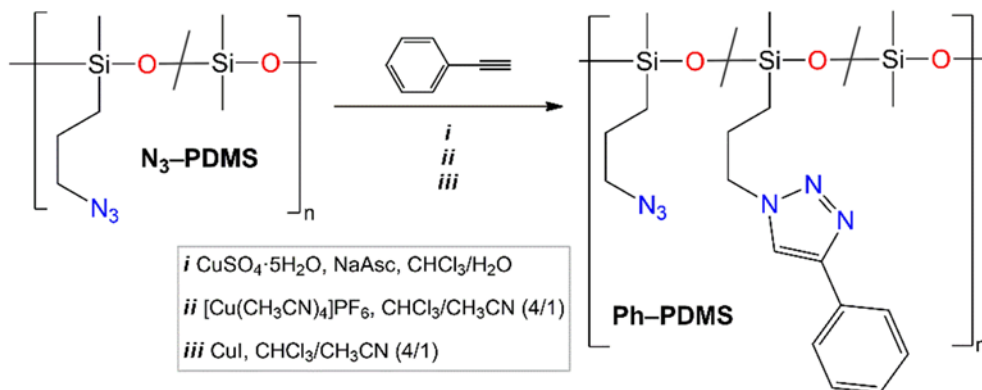


Figure S3. <sup>13</sup>C NMR spectrum of N<sub>3</sub>-PDMS.

## Optimization of the procedure for conducting the CuAAC reaction on a model system

To optimize the procedure, the N<sub>3</sub>-PDMS/phenylacetylene system was chosen as a model system. The effect of three different catalytic systems (*i–iii*) on the completeness of the reaction was studied (Figure S4).



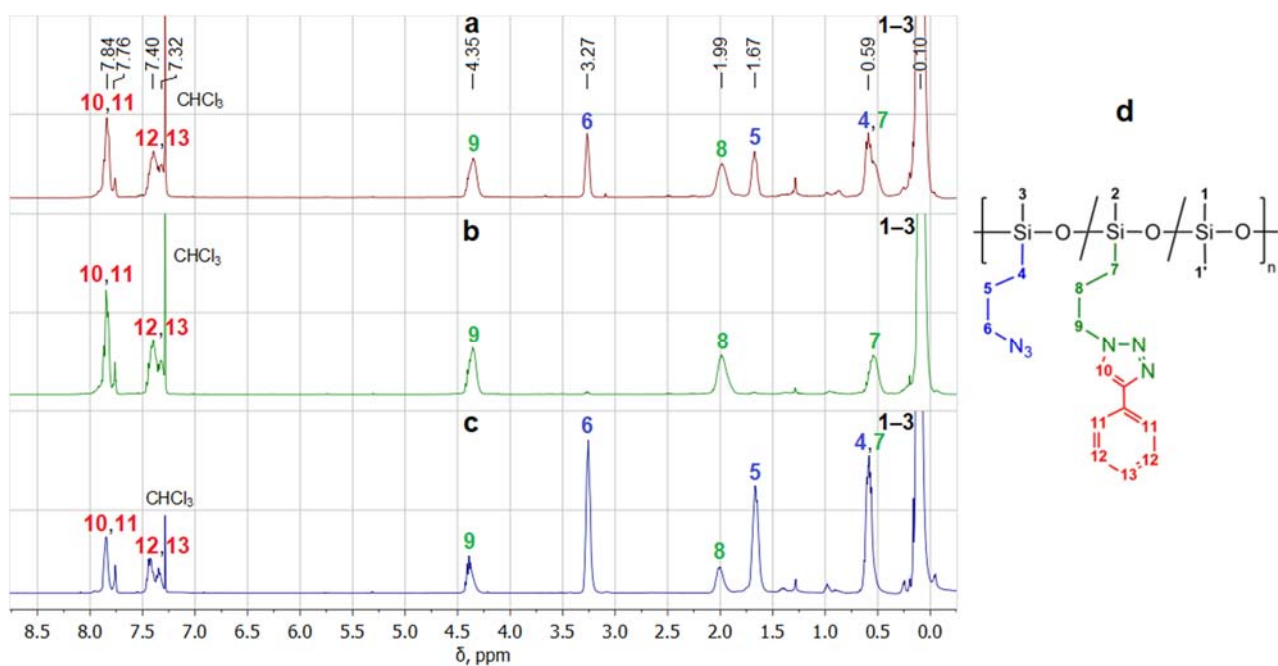
**Figure S4.** Optimization scheme for the click chemistry reaction.

Three different catalytic systems were used: the CuSO<sub>4</sub>·5H<sub>2</sub>O/sodium ascorbate system, as well as [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> and copper(I) iodide. It was experimentally found that to carry out a click reaction in a model system using [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> as a catalyst, a mixture of CHCl<sub>3</sub>/CH<sub>3</sub>CN in a 4:1 ratio, respectively, must be used as a reaction medium. Violation of this ratio leads to a decrease in the solubility of one of the components with the formation of the corresponding precipitate. Based on the results of the <sup>1</sup>H NMR spectroscopy analysis (Figure S5), the percentage of reacted azide groups for each system was established from the ratios of the integral intensities of the corresponding peaks (Table S1). [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> was chosen as the most effective catalyst, which in addition to efficiency allows the reaction to proceed in one phase.

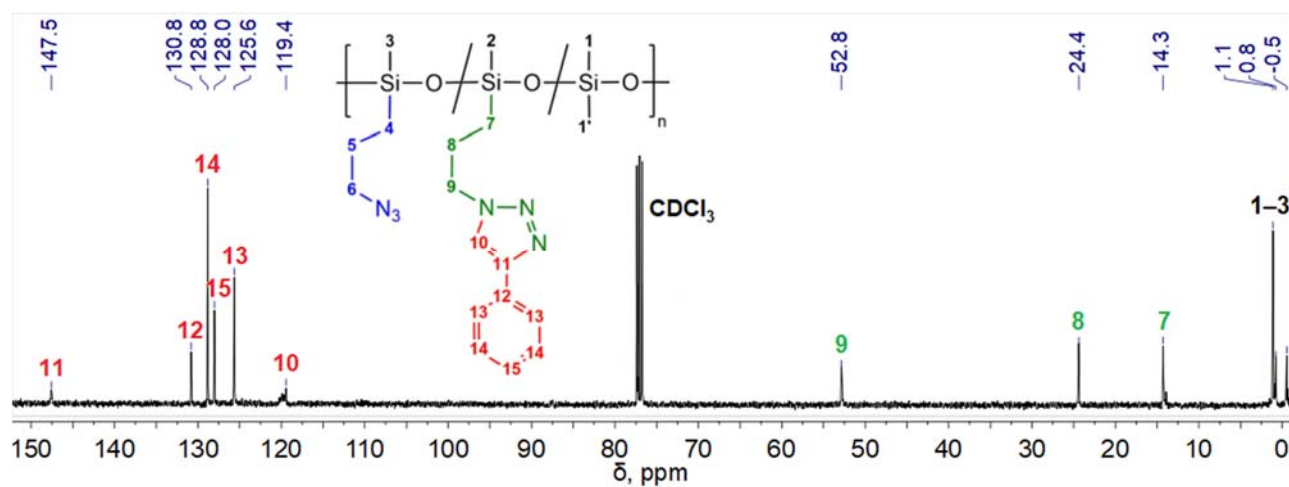
*Synthetic method of Ph-PDMS preparation.* 350 mg of N<sub>3</sub>-PDMS (0.96 mmol of N<sub>3</sub>-containing units) and 98 mg (0.96 mmol) of phenylacetylene were dissolved in 30 ml of CHCl<sub>3</sub>. The resulting solution was mixed with catalyst which was previously dissolved in 7.5 ml of CH<sub>3</sub>CN: (*i*) 240 mg (0.96 mmol) of CuSO<sub>4</sub>·5H<sub>2</sub>O and 380 mg (1.92 mmol) of sodium ascorbate dissolved in water, or (*ii*) 358 mg (0.96 mmol) of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub>, or (*iii*) 183 mg of (0.96 mmol) CuI. The mixture was refluxed with vigorous stirring for 24 h. In the case of CuSO<sub>4</sub>·5H<sub>2</sub>O/sodium ascorbate system the organic phase was separated, then washed twice with water and filtered off. The resulting solution was washed with a saturated water solution of Trilon B, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and filtered off. The solvent was removed under reduced pressure (20 mbar, 55 °C) using a rotary evaporator. Yields: 383 mg (86%, CuSO<sub>4</sub>·5H<sub>2</sub>O/sodium ascorbate catalytic system), 408 mg (91%, [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> catalytic system), and 323 mg (72%, CuI catalytic system). NMR data are presented below (Figure S5, Figure S6).

**Table S1.** Comparison of the efficiency of catalytic systems.

Catalyst	Percentage of reacted N <sub>3</sub> -groups
CuSO <sub>4</sub> ·5H <sub>2</sub> O/sodium ascorbate	55%
[Cu(CH <sub>3</sub> CN) <sub>4</sub> ]PF <sub>6</sub>	97%
CuI	23%

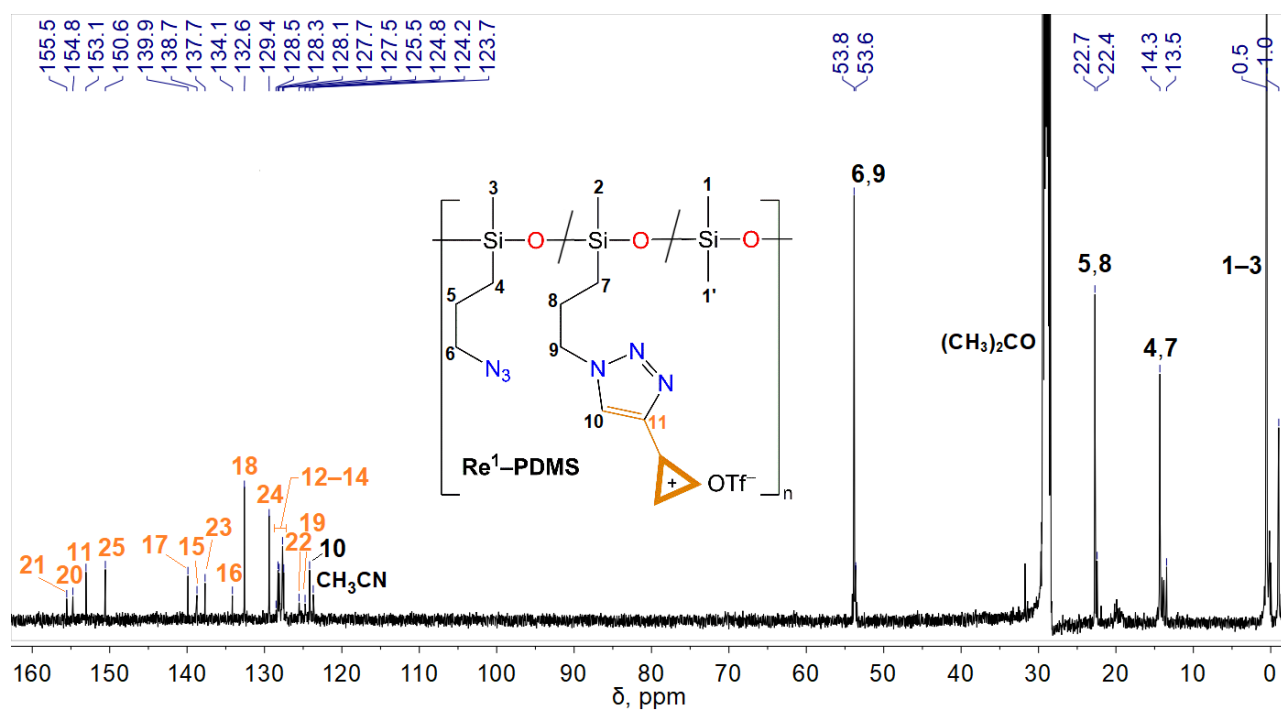


**Figure S5.** Superimposed  $^1\text{H}$  NMR spectra of the resulting polymers for each of the three reaction systems based on  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ /sodium ascorbate (a),  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (b), and  $\text{CuI}$  (c).



**Figure S6.**  $^{13}\text{C}$  NMR spectrum of Ph-PDMS ( $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  catalytic system).

# <sup>13</sup>C NMR spectrum of Re1-PDMS



**Figure S7.** <sup>13</sup>C NMR spectrum of Re1-PDMS (after 5-day reaction). Resonances 12–25 are assigned to Re moiety.