Supporting Information

**Design Principles of Chemiluminescence Chemodosimeter for Self-Signaling Detection: Luminol Protective Approach**

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**Synthetic details.** TBS-luminol and TIPS-luminol were synthesized according to the procedure shown in Scheme S1 and Scheme S2, respectively. All chemicals purchases commercially, and used without further purification. The progress of reaction was checked on TLC plates (Merck 5554 Kiesel gel 60 F254), and the spots were visualized under 254 nm UV light and/or charring after dipping the TLC plate into vanillin solution (9.0 g of vanillin and 1.5 mL of concentrated sulfuric acid in 300 mL of MeOH) and KMnO₄ solution (3 g of KMnO₄, 20 g of K₂CO₃, and 5 mL of 5% NaOH solution in 300 mL of water). Column chromatography was performed on silica gel (Merck 9385 Kiesel gel 60). Unless otherwise specified, all reactions were conducted under a slight positive pressure of dry nitrogen. The usual work-up refers to washing the quenched reaction mixture with brine, drying the organic extracts over anhydrous MgSO₄ and evaporating under reduced pressure using a rotary evaporator.

**Spectroscopic Characterization.** ^1^H-NMR, ^13^C-NMR, 2D NOESY NMR, and 2D HMBC NMR spectra were recorded on a Varian, MR 400 (400 MHz) in DMSO solution. Chemical shift values were recorded as parts per million relative to tetramethylsilane as an internal standard, and coupling constants in Hertz. Mass spectra were recorded on an Agilent Q-TOF 6520 system using electrospray in positive ion detection (ESI+) mode. Significant fragments are reported in the following fashion: m/z (relative intensity). Elemental analysis was carried out using a CE instruments, EA1110 elemental analyzer. UV-visible absorption spectra were measured on a Varian Cary50 UV/Vis
spectrophotometer. Chemiluminescence and Time-dependent chemiluminescence were obtained using PTI Quanta Master TM spectrofluorometers equipped with an integrating sphere and an laser excitation system.

**Calculation details.** DFT calculations are used to rationalize the reaction path for the synthesis of TBS-Luminol from Luminol in aqueous media under basic condition (pyridine).

\[ \text{Lum + Py + TBSCl} \rightarrow \text{IM + PyH}^+ + \text{TBSCl} \rightarrow \text{TBS-Lum + Py + HCl} \]

All possible reactants, intermediates and products were geometry optimized by density functional theory (DFT) in water, described by the Polarizable Continuum Model (PCM) as implemented in the Gaussian09 program package.\(^1\) Since the geometry might be a critical issue, all calculations were done without symmetry constraints using the BHandHLYP functional. For comparison, the B3LYP was used which yield very similar results. The absolute geometries were confirmed by the absence of negative frequencies in the respective frequency calculations, which also yield the free Gibbs energies \(\Delta G\). Comparison of \(\Delta G\) for reactants, intermediates (IM) and products were obtained by applying Hess's law.

**The reaction conditions and injection sequence of TBS-luminol and luminol for CL measurements.** Addition of tetrahydrofuran (THF) solution of TBS-luminol or luminol \((1.7 \times 10^{-3} \text{ M, } 200 \mu l)\) to a mixed water solution of \(\text{Co(NO}_3\text{)}_2 (5 \times 10^{-4} \text{ M, } 400 \mu l)\), \(\text{H}_2\text{O}_2 (2 \times 10^{-2} \text{ M, } 400 \mu l)\) and \(\text{Na}_2\text{CO}_3/\text{NaHCO}_3 (1.0 \times 10^{-1} \text{ M, } 400 \mu l)\).

**The evaluation of the performance of TBS- and TIPS-luminol as a sensor of F⁻.** We used

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tetrabutylammonium fluoride (TBAF, $1 \times 10^{-1}$ M, 100 μl) as a F$^-$ source and added TBAF into the THF solution of TBS-luminol (3.4×$10^{-3}$ M, 100 μl) or TIPS-luminol (3.4×$10^{-3}$ M, 100 μl). Subsequent exposure of the resulting solution to the mixed water solution of Co(NO$_3$)$_2$ (5×$10^{-4}$ M, 400 μl), H$_2$O$_2$ (2×$10^{-2}$ M, 400 μl) and Na$_2$CO$_3$/NaHCO$_3$ (1.0 ×$10^{-1}$ M, 400 μl) produced strong blue CL emission,
**Scheme S1.** The synthetic scheme of TBS-luminol

**TBS-luminol** tert-Butylsilyl chloride (5.11 g, 33.9 mmol) was added to a solution of luminol (2.0 g, 11.3 mmol) in pyridine (9.0 ml) at room temperature. The solution was stirred at room temperature for overnight. The reaction mixture was poured into water and extracted with ethyl acetate and washed with water and brine. The organic phase was dried over MgSO$_4$ and the solvent was evaporated in vacuo. Purification of the residue by column chromatography (hexanes-ethyl acetate, 10:1) provided TBS-luminol (2.1 g, 64 %).

$^1$H NMR (400 MHz, DMSO-d$_6$): δ 11.35 (s, 1 H), 7.50 (t, 1 H, $J$ = 7.8 Hz), 7.35 (br s, 2 H), 6.89 (d, 2H, $J$ = 7.5 Hz), 1.00 (s, 9H), 0.30 (s, 6H).

$^{13}$C NMR (100 MHz, DMSO-d$_6$): δ 161.7, 150.8, 149.3, 134.2, 127.1, 116.4, 110.5, 108.8, 25.7, 17.8, -4.6. HRMS (ESI$^+$) calcd. for C$_{14}$H$_{21}$N$_3$O$_2$Si (M$^+$+1) 292.1476, found 292.1482.

**Scheme S2.** The synthetic scheme of TIPS-luminol

**TIPS-luminol** Triisopropyl silyl chloride (6.53 g, 33.9 mmol) was added to a solution of luminol (2.0 g, 11.3 mmol) in pyridine (9.0 ml) at room temperature. The solution was stirred at room temperature for overnight. The reaction mixture was poured into water and extracted with ethyl acetate and washed with water and brine. The organic phase was dried over MgSO$_4$ and the solvent was evaporated in vacuo. Purification of the residue by column chromatography (hexanes-ethyl acetate, 10:1) provided TIPS-luminol (2.5 g, 67 %).

$^1$H NMR (400 MHz, DMSO-d$_6$): δ 11.42 (s, 1 H), 7.51 (t, 1 H, $J$ = 8.0 Hz), 7.34 (br s, 2 H), 6.89 (d, 2H, $J$ = 7.5 Hz), 6.90 (d, 1H, $J$ = 8.0 Hz), 1.00 (s, 9H), 1.42 – 1.41 (m, 3H), 1.08 (d, 18H, $J$ = 8.0 Hz).

$^{13}$C NMR (100 MHz, DMSO-d$_6$): δ 161.8, 150.9, 149.0, 134.2, 126.9, 116.4, 110.5, 108.8, 17.8, 12.1. HRMS (ESI$^+$) calcd. for C$_{14}$H$_{21}$N$_3$O$_2$Si (M$^+$+1) 333.1873, found 333.1879.
Figure S1. $^1$H-NMR spectra of (a) TBS-luminol and (b) luminol registered in DMSO-d$_6$. $^{13}$C-NMR spectra of (c) TBS-luminol and (d) luminol registered in DMSO-d$_6$.
Figure S2. Chemiluminescence (CL) spectra of (a) TBS-luminol and (b) Luminol depending upon addition of base.

Figure S3. CL spectra of (a) TIPS-luminol and (b) Luminol depending upon addition of base.
Figure S4. UV-Vis spectra of the luminol derivatives before and after adding tetrabutylammonium hydroxide (TBAOH). Experimental conditions are as follows: luminol derivatives (3.4 X 10^{-3} M in THF, 0.1 mL), THF (0.6 mL), DI-water (0.6 mL), and TBSOH (1 M, 0.04 mL).

Figure S5. (a) CL intensity curves of TBS-luminol were plotted versus time at various TBAF concentrations, (b) linear calibration data for F⁻ concentration.
**Figure S6.** (a) CL intensity curves of TIPS-luminol were plotted versus time at various TBAF concentrations, (b) linear calibration data for F⁻ concentration.

**Figure S7.** UV-Vis spectra of TIPS-luminol (THF, 1.1×10⁻⁵ M) and TBAF (THF, 1.1×10⁻⁵ M) treated TIPS-luminol with different incubation time were plotted.
Figure S8. Relative integrated CL intensity of TIPS-luminol (THF, $1.1 \times 10^{-5}$ M; DMSO, $1.1 \times 10^{-5}$ M) after treatment of excess amount of TBAF, KF, and CsF ($7.1 \times 10^{-4}$M).