

Supporting information

Electrochemical and magnetic properties of a surface-grafted novel endohedral metallofullerene derivative

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Table of Contents

Experimental procedures.....	S2
Reference for the Supporting information.....	S4
Figure S1. HPLC profiles of the crude reaction mixture of 2	S5
Figure S2. HPLC profiles of multi-steps separation.....	S5
Figure S3. HPLC profiles of isolated 2a and 2b	S6
Figure S4. MALDI-TOF mass spectra of 2a and 2b	S7
Figure S5. ESR spectra of 2a and 2b	S7
Table S1. g-Value and hfcc of 2a and 2b	S8
Figure S6. ¹ H NMR spectrum of anionic 2b	S8
Figure S7. Vis-NIR absorption spectra of 2a , 2b and reference compounds.....	S9
Figure S8. Schematic drawing of the isomers.....	S10
Figure S9. CV of 2b in solution.....	S10
Figure S10. AFM images of the La@C ₈₂ -S-Au SAM.....	S11
Figure S11. XPS of La3d and S2p for the La@C ₈₂ S-Au SAM.....	S12
Figure S12. TOF-SIMS of the La@C ₈₂ -S-Au SAM.....	S13
Figure S13. Cyclic voltammetry of the La@C ₈₂ -S-Au SAM.....	S14
Figure S14. ESR spectrum of the drop-casted film of La@C ₈₂ (2b) on gold.....	S15

Experimental Procedures

General for the synthesis and characterization of compounds. All chemicals and solvents were obtained from Wako Inc. or Sigma-Aldrich Inc. and used without further purification unless otherwise stated. $\text{La}@C_{2v}\text{-C}_{82}^{[1]}$ was prepared according to the reported procedures. *o*-Dichlorobenzene was distilled over calcium hydride at reduced pressure under an argon atmosphere before use in reactions. Analytical high-performance liquid chromatography (HPLC) was performed on a HPLC apparatus (LC-2000 series; Jasco Inc.) using 5PYE, Buckyprep, Buckyprep M, or 5PBB columns (4.6 × 250 mm; Nacalai Tesque Inc.) Preparative HPLC was performed on a HPLC apparatus (LC-9204 ; Japan Analytical Industry Co., Ltd.) using 5PYE, Buckyprep, or 5PBB columns (20 × 250 mm; Nacalai Tesque Inc.). They were monitored with UV absorption at 330 nm, and toluene was used as the eluent. The $^1\text{H-NMR}$ measurements were conducted on a spectrometer (AVANCE 500; Bruker Analytik GmbH) with a CryoProbe system, or a spectrometer (AVANCE 300) where TMS was used as an internal reference ($\delta = 0.00$ ppm). Absorption spectra were recorded using a spectrophotometer (UV-3150; Shimadzu Corp.). Mass spectrometry was conducted using a mass spectrometer (BIFLEX III; Bruker Analytik GmbH) with 1,1,4,4-tetraphenyl-1,3-butadiene as a matrix. Cyclic voltammograms (CVs) and differential pulse voltammograms (DPVs) were recorded using an electrochemical analyzer (ALS630D; BAS Inc.). Platinum wires were used as the working and counter electrodes. The reference electrode was a saturated calomel reference electrode (SCE) filled with 0.1 M (*n*-Bu) $_4$ NPF $_6$ (TBAPF $_6$) in *o*-DCB. All potentials are referenced to the ferrocene/ferrocenium couple (Fc/Fc $^+$) as the standard. CVs were recorded using a scan rate of 50 mV/s, and DPVs were obtained using a pulse amplitude of 50 mV, a pulse width of 50 ms, a pulse period of 200 ms, and a scan rate of 20 mV/s. The solution was deaerated for 20 min. with argon before electrochemical measurements. Electron paramagnetic resonance (EPR) spectra in solution were recorded by a Bruker EMXPlus9.5/2.7. The spectrometer was operated at 9.8 GHz with a microwave power of 0.2 mW (30 dB), a modulation frequency of 100 kHz, and modulation amplitude of 300 mG. The *g* values were determined by the readout function of the spectrometer with the weak pitch as a standard, while the hyperfine splitting constants were measured using a Hall unit for calibration of the magnetic field.

Synthesis of a thioacetate-terminated aldehyde (1). To a 2 M NaOH aqueous solution (100 mL) of 4-hydroxybenzaldehyde (3.66 g, 30.0 mmol), 1,4-dibromobutane (7.77 g, 36.0 mmol) was added, and then refluxed and stirred vigorously under argon atmosphere. After 24 hrs, organic phase was separated and aqueous phase was extracted three times with CH_2Cl_2 (8 mL). The organic phases were combined and washed once with 2 M HCl aq. (10 mL) and twice with H_2O (10 mL). The organic solution was dried with MgSO_4 and solvent was removed under a reduced pressure. Obtained yellow oil was dissolved in dry THF (70 mL) and potassium thioacetate was added to the solution. Then the solution was refluxed under argon atmosphere for 16 hrs. After cooling, the solution was filtered and solvent was removed under a reduced pressure from the

filtrate. Obtained dark yellowish green oil was separated by silica gel chromatography using hexane/Et₂O (3/1 = v/v) as an eluent, and **1** was obtained as red oil ($R_f = 0.56$, 1.07 g, 4.23 mmol, 14 % yield)

¹H NMR (300 MHz, acetone-*d*₆, 293 K, δ) 9.87 (s, 1H), 7.82 (d, 2H, $J = 14.5$ Hz), 6.98 (d, 2H, $J = 14.5$ Hz), 4.05 (t, 2H, $J = 10$ Hz), 2.95 (t, 2H, $J = 12$ Hz), 2.34 (s, 3H), 1.89 (m, 2H), 1.78 (m, 2H). ¹H NMR (500 MHz, CDCl₃, 293 K) $\delta = 9.83$ (s, 1H), 7.77 (d, 2H, $J = 14.5$ Hz), 6.94 (d, 2H, $J = 14.5$ Hz), 4.01 (t, 2H, $J = 10$ Hz), 2.90 (t, 2H, $J = 12$ Hz), 2.29 (s, 3H), 1.84 (m, 2H), 1.73 (m, 2H). ¹³C NMR (125 MHz, CDCl₃, 293 K, δ) = 190.6, 163.8, 131.8, 129.6, 114.5, 67.5, 28.5, 27.9, 26.1. ESI-Mass [M^+] calcd. 252.082, found 252.082 m/z.

Synthesis of La@C82CMe2NMeCHC6H4OC4H8SCOMe (2a and 2b). o-DCB (50 mL) solution containing 5.00 mg of La@C2v-C82 (5.00 mg, 4.46 μ mol) was carefully degassed and heated at 145°C with 2-methylaminoisobutyric acid (20.4 mg, 150 μ mol) and **1** (see SI for synthetic procedure) (14.6 mg, 50.0 μ mol) under argon atmosphere. After heating for 18 min, the reaction mixture was separated by multi-step HPLC procedure for the isolation of the target compound from byproducts and unreacted starting materials. The profiles are shown in Figure S2. As the result, **2a** and **2b** were obtained in 21% and 67% yields, based on the consumed starting fullerene, which were estimated by the HPLC analyses.

2a (The minor product): UV-vis-NIR (CS₂) $\lambda_{max} = 1032, 1479$ nm. MALDI-TOF MS calculated for C₉₉H₂₅LaNO₂S ([M]⁻): 1430.07, found: 1430.1 m/z.

2b (The major product): UV-vis-NIR (CS₂) $\lambda_{max} = 1034, 1488$ nm. MALDI-TOF MS calculated for C₉₉H₂₅LaNO₂S ([M]⁻): 1430.07, found: 1430.1 m/z.

Note: We found that -SH groups may react with La@C₈₂ at high temperature, such as a condition for the Prato reaction. Therefore, we used the less reactive -S(CO)CH₃ group instead of -SH group for the preparation of **2a** and **2b**.

Preparation of the anionic 2b by bulk electrolysis. Controlled-potential bulk electrolysis was performed using an H-type cell with two platinum gauze electrodes as the working and counter electrodes. [**2b**]⁻ was obtained under argon in ODCB containing 0.2 M TBAClO₄ by setting the applied potential at a value 300 mV more negative than the E_{1/2} value of the [**2b**]⁻/**2b** redox couple. The excess supporting electrolyte was precipitated from the solvent by adding carbon disulfide to the ODCB and then removed by filtration. The solvent was evaporated under reduced pressure. The residual brown solid was washed with 1-propanol, dried again, and dissolved in 1:1 (v/v) acetone-*d*₆/CS₂ for NMR analysis.

[TBA]⁺[**2b**]⁻: ¹H NMR (500 MHz, CS₂/acetone-*d*₆, 1/1, 293 K, δ) 7.51 (d, $J = 7.0$ Hz, 1H), 7.46 (d, $J = 7.0$ Hz, 1H), 6.83 (d, $J = 7.0$ Hz, 1H), 6.78 (d, $J = 7.0$ Hz, 1H), 3.96 (t, $J = 6.0$ Hz, 2H), 3.92 (s, 1H), 3.39-3.36 (TBA⁺, t, $J = 8.0$ Hz, 8H), 2.91 (t, $J = 7.0$ Hz, 2H), 2.27 (s, 3H), 2.21 (s, 3H), 2.13 (m, 2H), 1.85 (m, 4H), 1.79-1.72 (TBA⁺,

quintet, $J = 8.0$ Hz, $J = 7.5$ Hz, 8H), 1.42-1.35 (TBA+, m, $J = 7.5$ Hz, 8H), 1.27 (s, 3H), 1.20 (s, 3H), 0.97-0.94 (TBA+, t, $J = 7.5$ Hz, 12H). UV-vis-NIR (ODCB) $\lambda_{\text{max}} = 613$, 936 nm.

General for the characterization of self-assembled monolayers (SAMs): All solvents used were of high purity grade for HPLC from ROMIL-SpS (Super Purity Solvent). Gold (111) substrates consisting of 300 nm Au on mica were purchased from Georg Albert PVD-Beschichtungen. The substrates were first rinsed with dichlorometane, acetone and ethanol and dried under nitrogen stream. Then, these substrates were cleaned in a UV ozone chamber for 20 minutes and afterwards immediately immersed in ethanol for at least 30 minutes, rinsed with ethanol and isopropanol and dried under N₂ stream. The substrates were immediately immersed in the solution of **2b**. SAM formation was carried out under light exclusion and under nitrogen atmosphere. See main text for detailed description of the preparation.

The electrochemical experiments were performed with a potentiostat/galvanostat 263a (EG&G Princeton Applied Research) using a platinum wire as counter electrode and a silver wire as a reference electrode. The gold surface modified with **2b** was used as a working electrode. XPS experiments were performed with a K-Alpha-Thermo Scientific with a monochromatic source Al K α line of 1486.68 eV with a perpendicular irradiation to the samples (90°). The analyzed spot size per point was 400 μm with an ellipsoidal disposition and an ion beam current of 6 mA. The experiments were performed at 2 E-7 mbar. For the general spectra a pass energy of 200 eV, a dwell time of 50ms and an energy step size of 1 eV were chosen. The conditions for specific elements, a pass energy of 40 eV, a dwell time of 50 ms and a energy step size of 0.1 eV were employed. The ToF-SIMS measurements were reordered with a TOF-SIMS⁵ (Time of Flight Secondary Ions Mass Spectrometer) under the following specific analysis conditions: primary gun energy of 25 KV, extractor energy of 8.5 KV, an emission current of 1.05 μA , employing Bi³⁺⁺ with an intensity of the primary ions of 0.25 pA. The experiments were performed in vacuum at 8.3 E⁻⁹ mbar. The spot size was 200 x 200 μm , with a resolution of 128 x 128 pixels, collecting above 1 E¹² of ionic intensity per spectrum.

EPR measurements were performed at room temperature using a Bruker ELEXYS E500 X-band spectrometer in a rectangular TE102 cavity. Precautions to avoid undesirable spectral distortions and line broadenings, such as those arising from microwave power saturation and magnetic field overmodulation, were also taken into account to improve sensitivity.

Atomic force microscopy images were acquired with SPM system from Agilent Technologies.

References:

[1] (a) K. Yamamoto, H. Funasaka, T. Takahashi, T. Akasaka, T. Suzuki, Y. Maruyama, *J. Phys. Chem.* **1994**, 98, 2008. (b) K. Yamamoto, H. Funasaka, T. Takahashi, T. Akasaka, *J. Phys. Chem.* **1994**, 98, 12831.

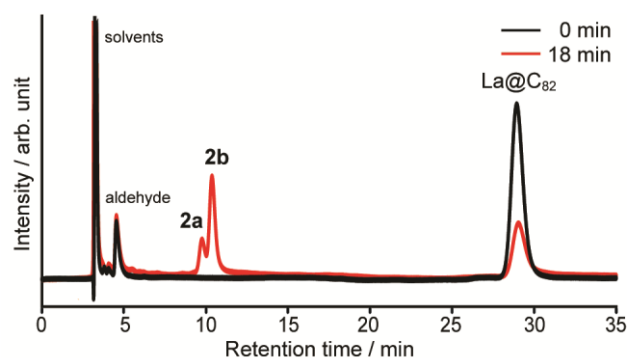


Figure S1. HPLC profiles of the reaction crude of **2**. Column: Buckyprep ϕ 4.6 \times 250 mm, eluent: toluene, flow rate: 1.0mL/min, wavelength: 330 nm, temperature: 40°C

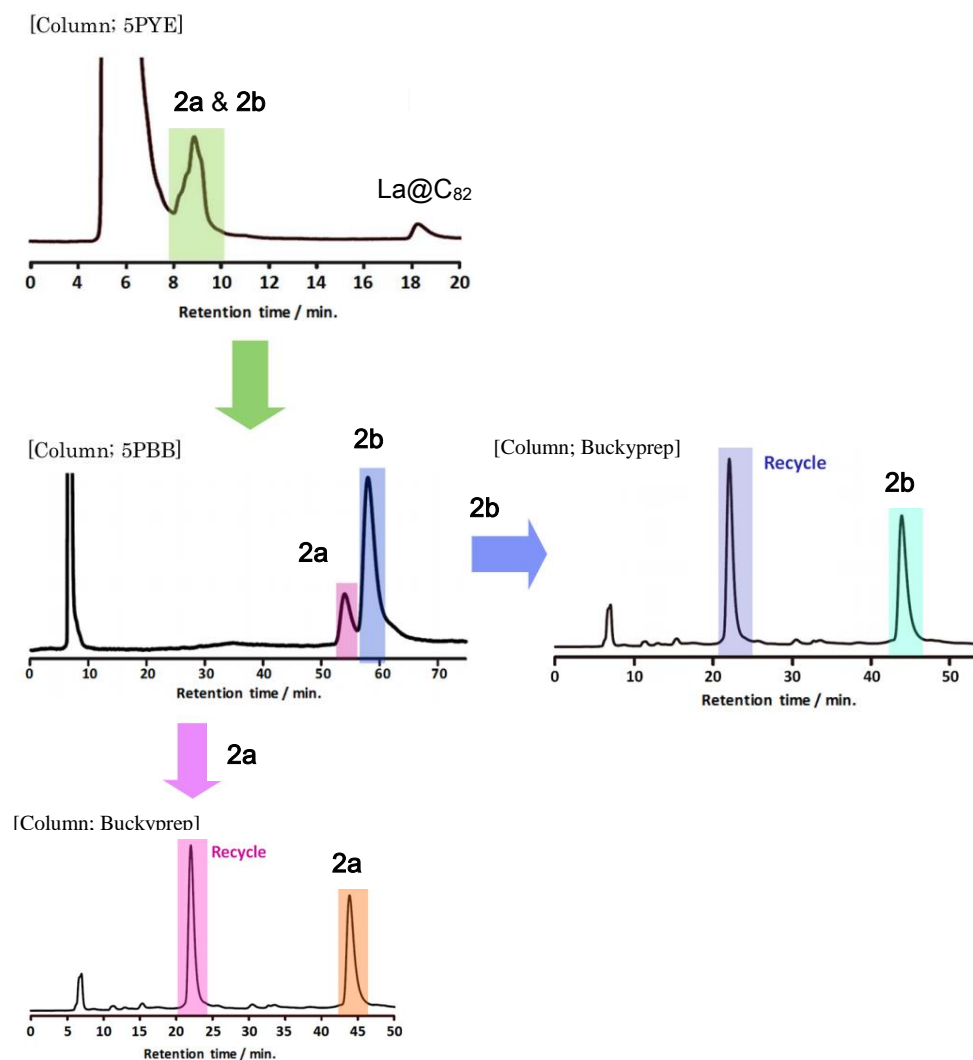


Figure S2. HPLC profiles of multi-step separations to isolate **2a** and **2b**. Column size: ϕ 10 \times 250 mm, Flow Rate: 9.99 mL/min, wavelength: 330 nm, temperature: r.t.

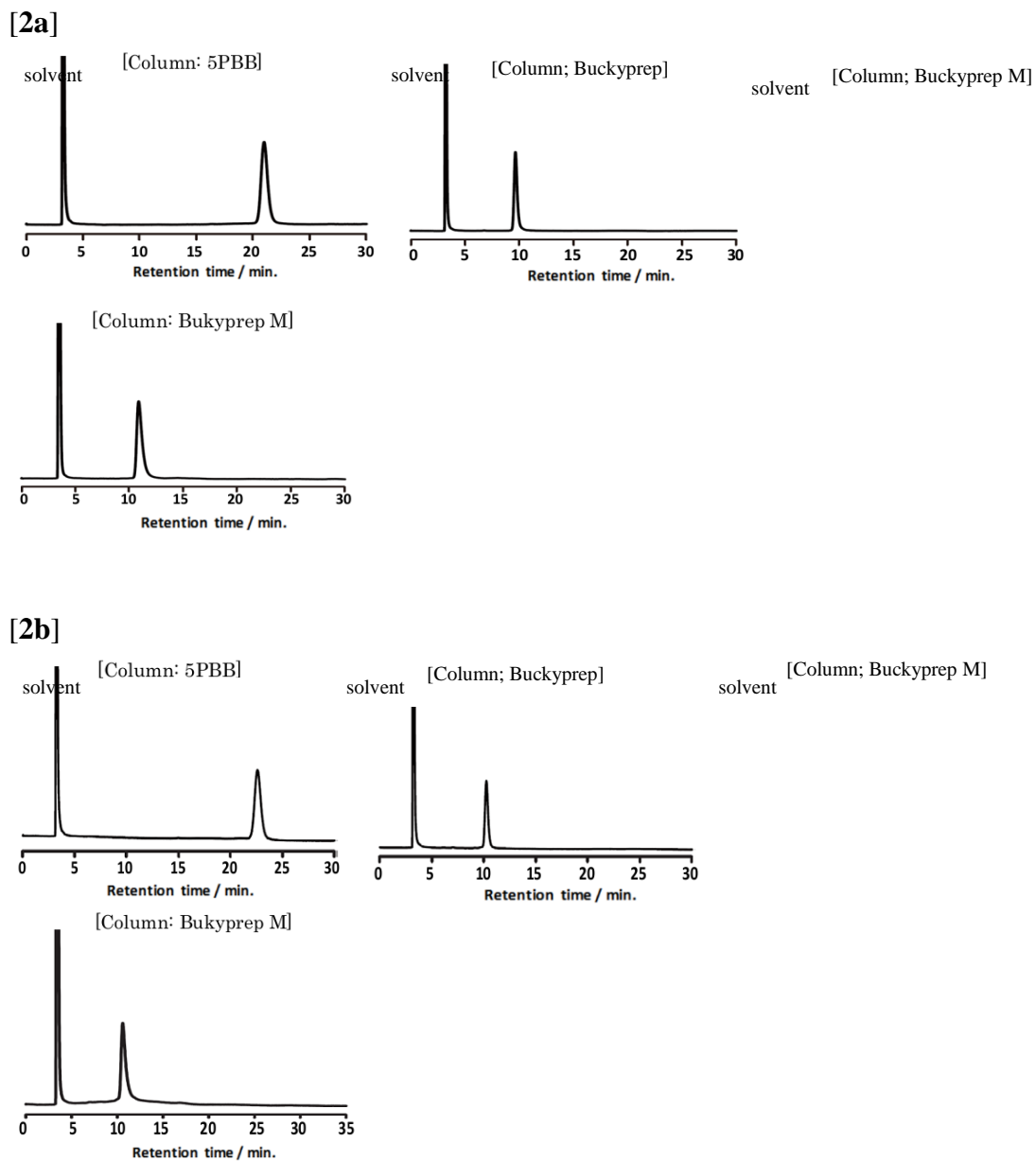
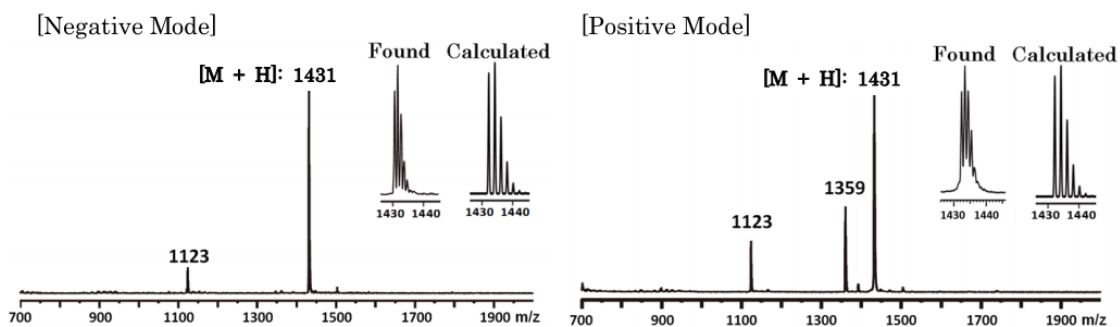


Figure S3. HPLC profiles of isolated (upper) **2a** and (bottom) **2b**. Column size: $\phi 4.6 \times 250$ mm, eluent: toluene, flow Rate: 1.0 mL/min, wavelength: 330nm, Temperature: 40°C

[2a]



[2b]

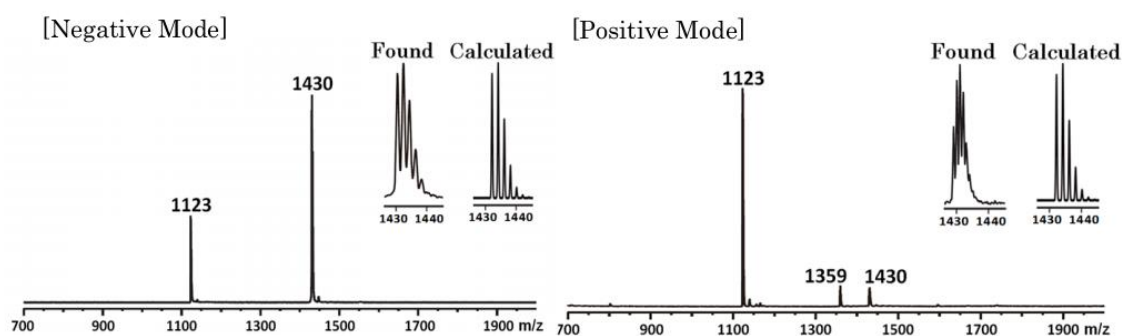


Figure S4. MALDI- TOF MS spectra of (upper) **2a** and (bottom) **2b**. (Left) Negative Mode, (Right) Positive Mode, Matrix: 1,1,4,4-Tetraphenyl-1,3-butadiene. The fragment peaks at 1123 and 1359 m/z are $La@C_{82}$ and **[2b -CMe₂NMe]**, respectively, which are caused by the laser desorption process in the observation of mass spectra.

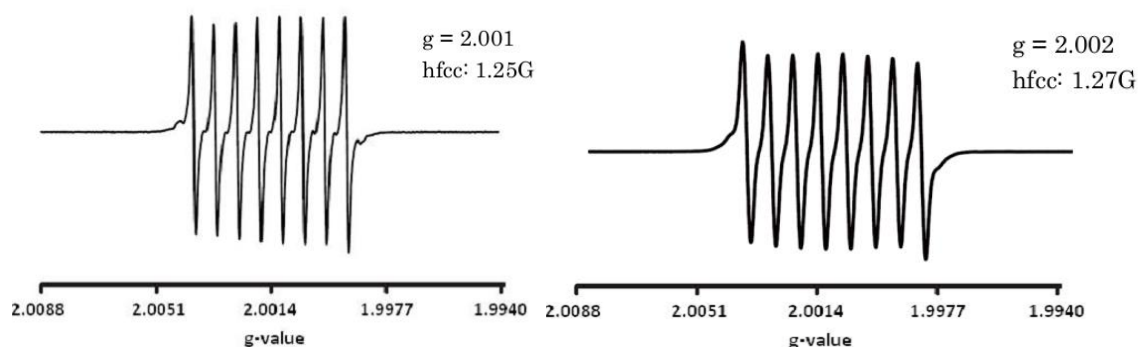


Figure S5. ESR spectra of (left) **2a** and (right) **2b**. Solvent: CS_2 , Temperature: r.t.

Table S1. g-Value and hfcc of **2a**, **2b** and pristine La@C₈₂ in CS₂

Compound	g-value	hfcc [G]
2a	2.001	1.25
2b	2.002	1.27
La@C ₈₂	2.001	1.15

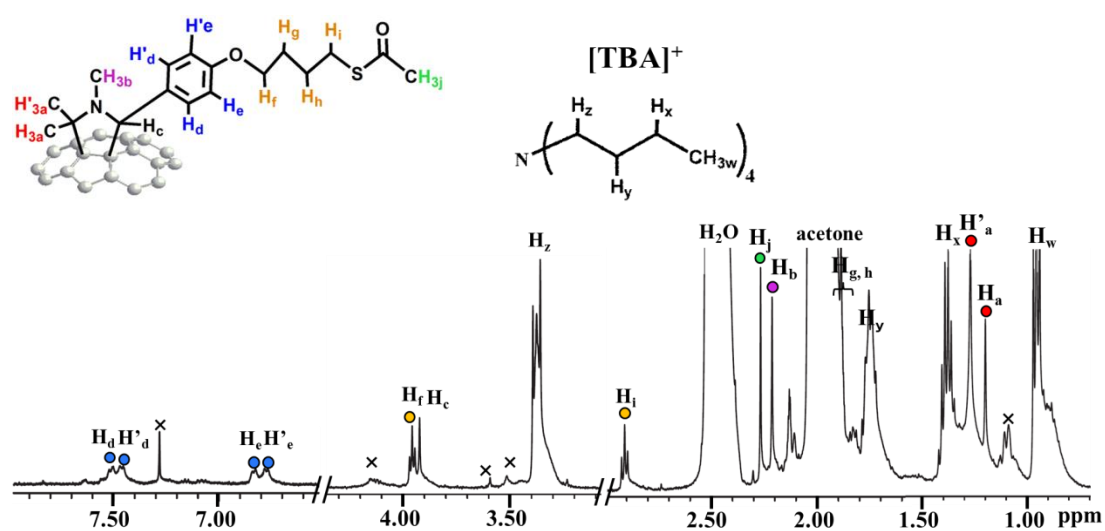


Figure S6. ¹H NMR spectrum of anionic **2b** at 500 MHz in 1:1 (v/v) acetone-*d*₆/CS₂ at 293 K. The signals from impurities were assigned based on the observation of blank solution containing possible impurities.

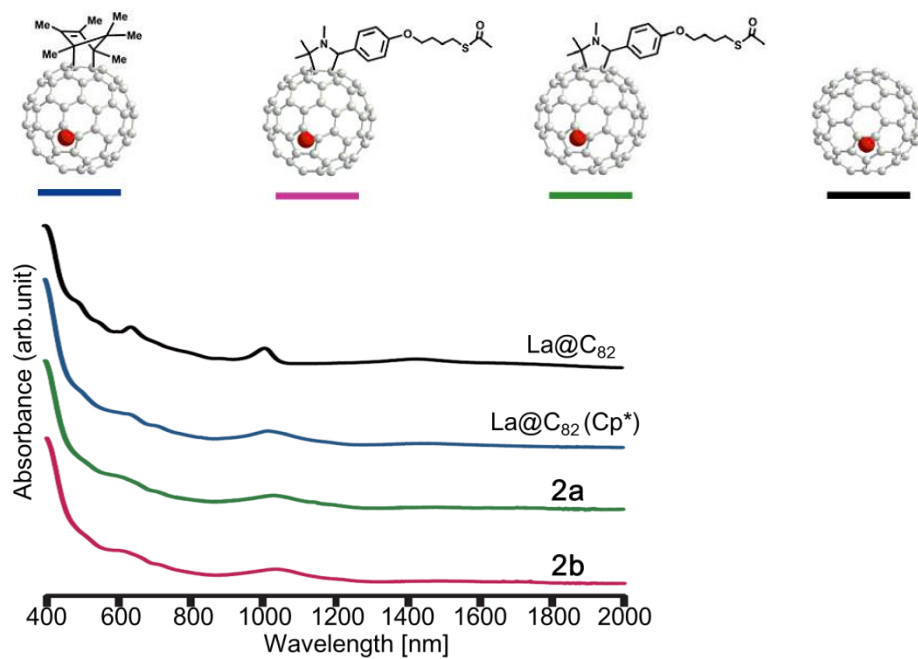


Figure S7. Vis-NIR absorption spectra of **2a**, **2b** and reference compounds in CS_2 .

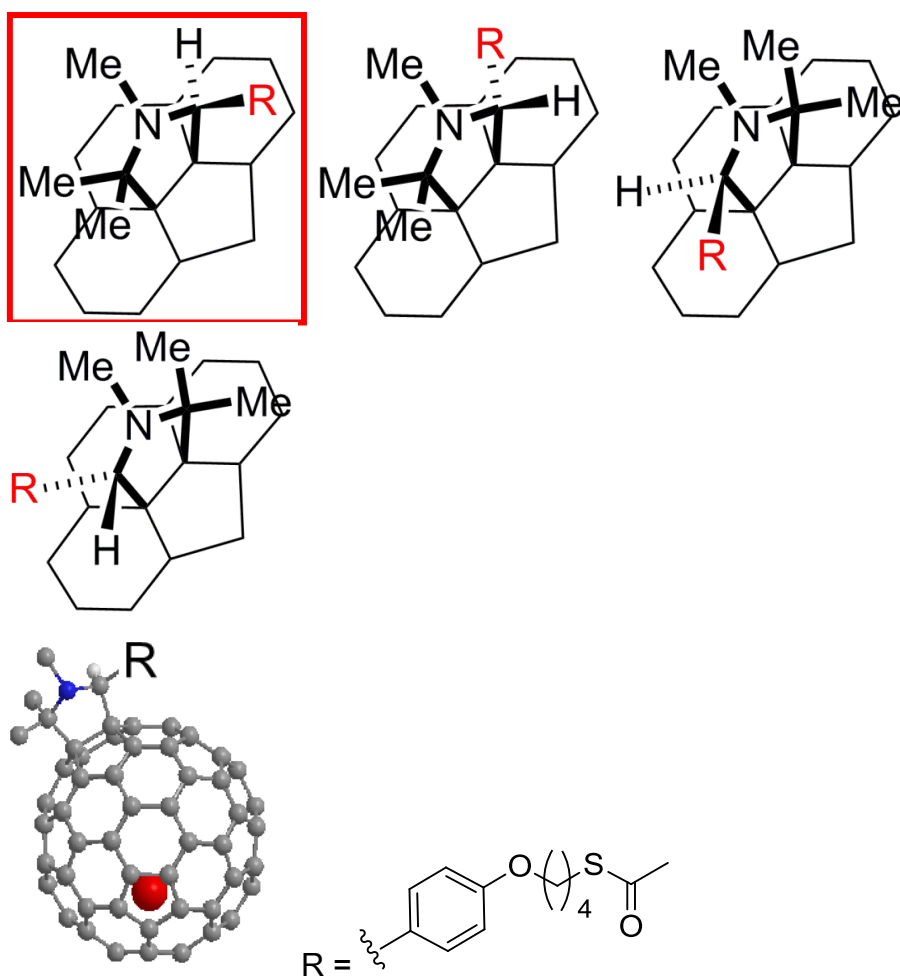


Figure S8. (Upper) Four possible addition patterns in the 1,3-dipolar cycloaddition reaction, where the most stable isomer is framed with red rectangle, and (bottom) schematic drawing of the most stable isomer. Relative stabilities are discussed on Ref.16 in the main text (Y. Takano, et al. J. Am. Chem. Soc. 2012, 134, 16103.).

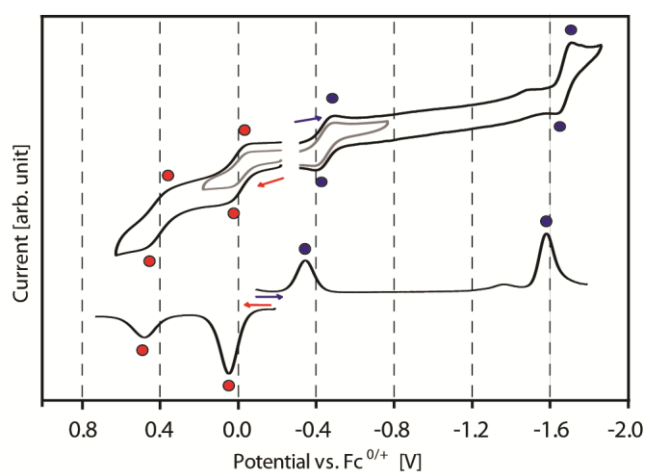


Figure S9. CV (upper) and DPV (lower) of 2b. TBAPF₆ 0.1 M in *o*-DCB was used as electrolyte, with a Ag/Ag⁺ electrode and platinum wires as a reference and working and counter electrodes, respectively (scan rate = 50 mV/s).

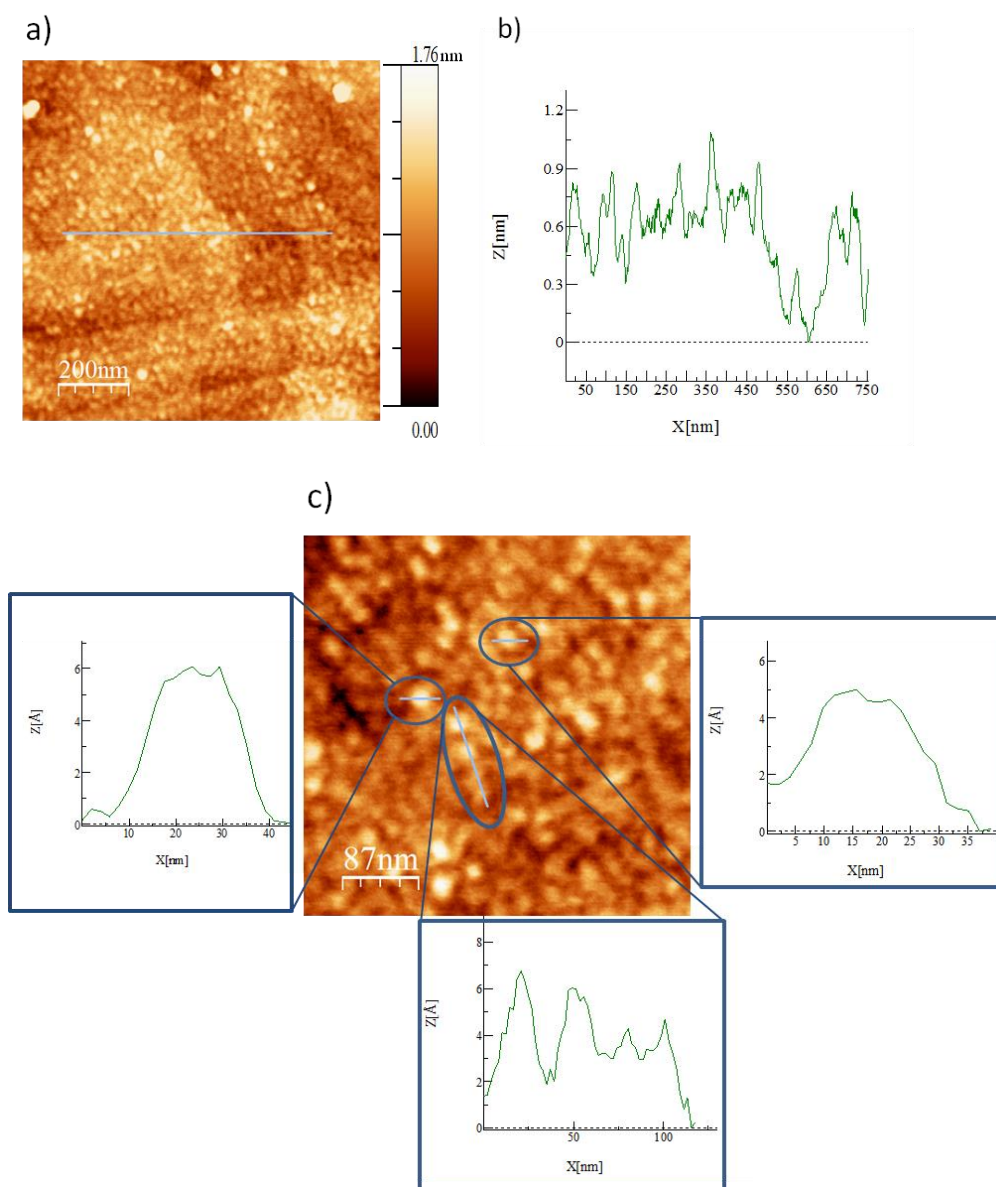


Figure S10. a) AFM topographic image (intermittent contact mode) of the La@C₈₂-S-Au SAM, which was prepared from 2b. b) Height profile (across the blue line in a). c) Digital zoom from image a) and the height profile of different round shape clusters.

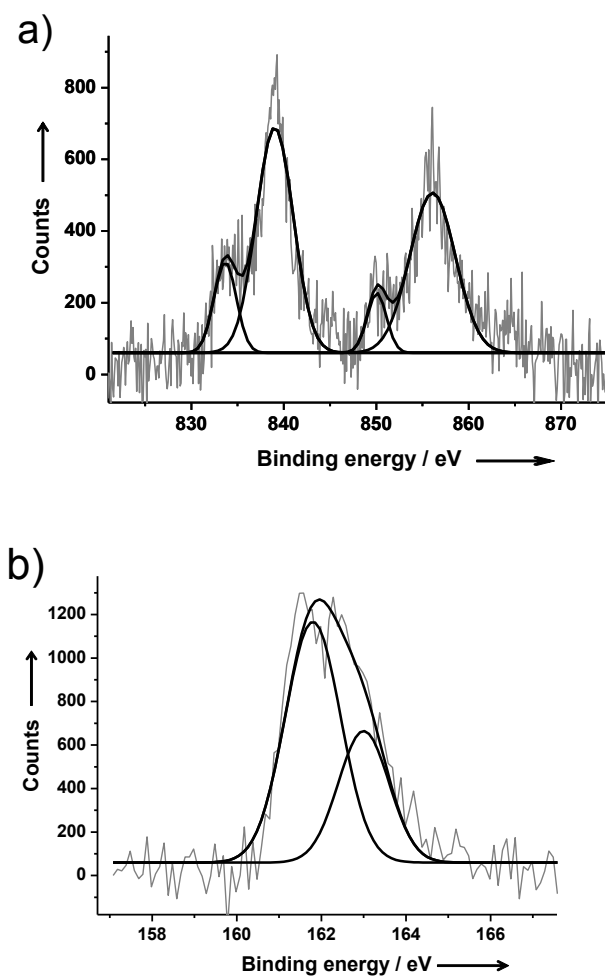


Figure S11. XPS of a) La3d and b) S2p for the La@C₈₂S-Au SAM.

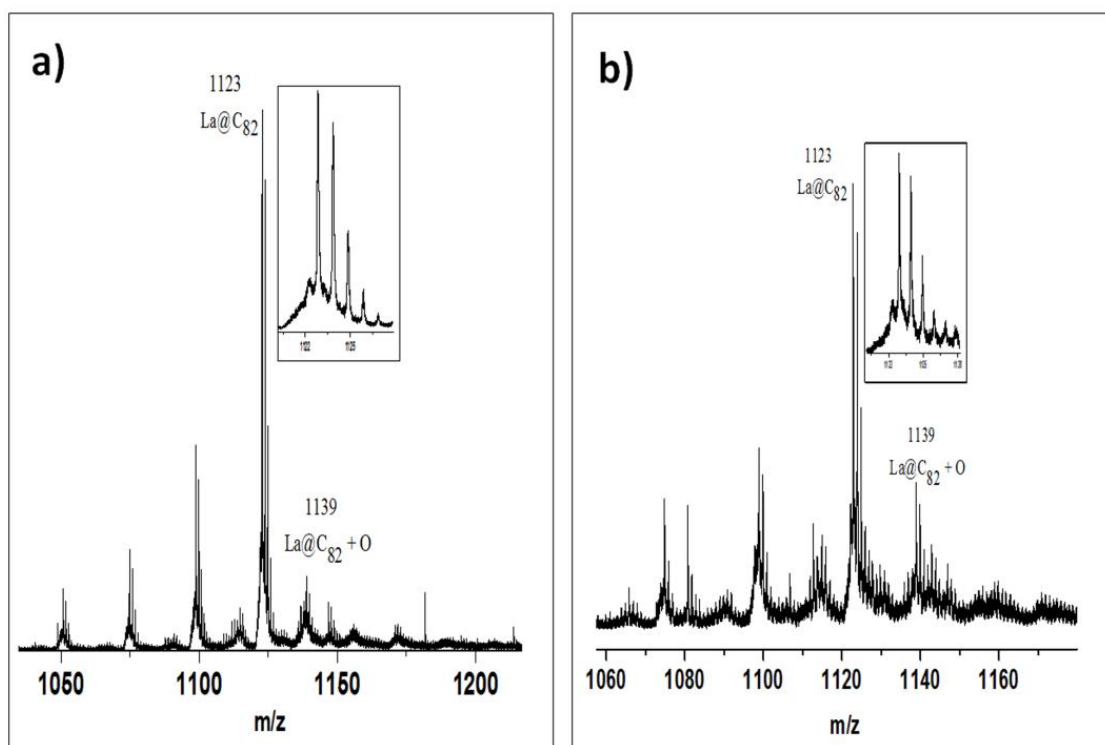


Figure S12. TOF-SIMS of the La@C₈₂-S-Au SAM: a) in positive and b) negative modes.

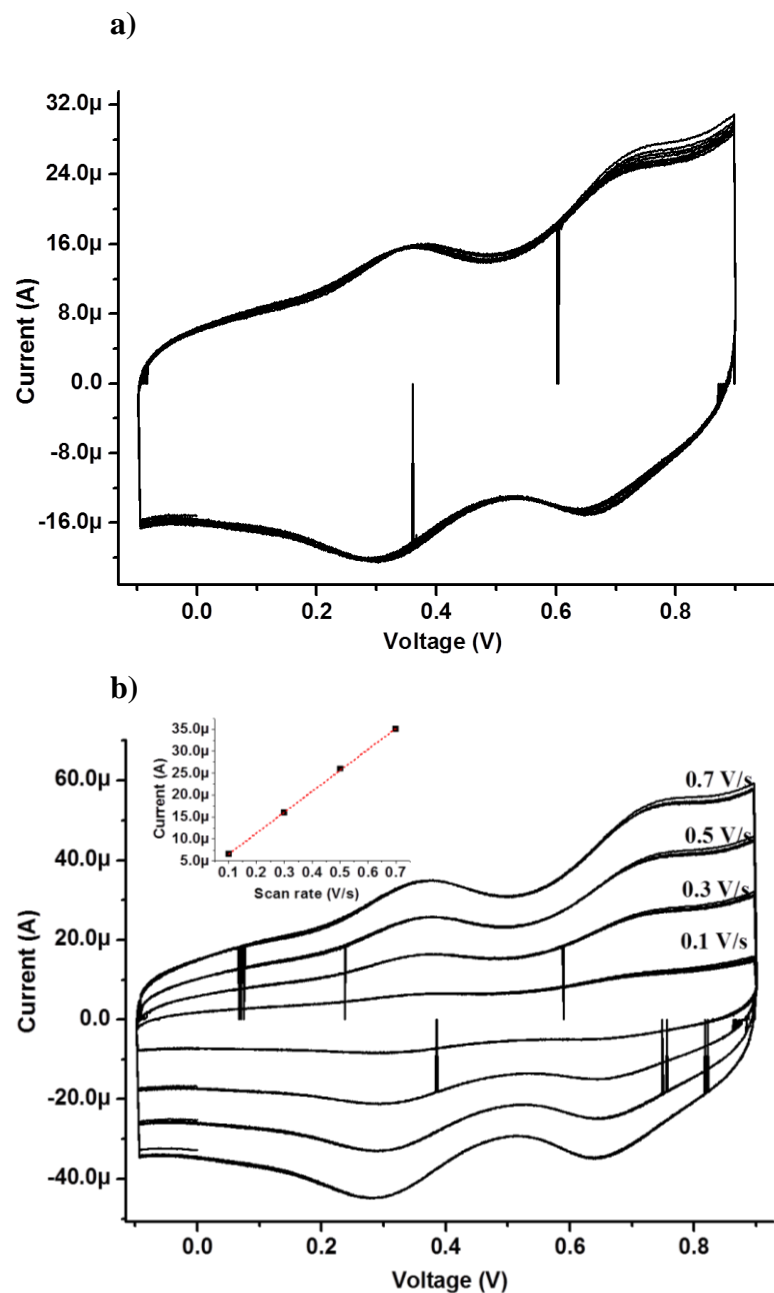


Figure S13. a) Cyclic voltammetry of the La@C₈₂-S-Au SAM recording ten consecutive cycles in the range of -0.1 to 0.9 V with a scan rate of 0.3 Vs⁻¹. Both experiments were carried out with *n*-Bu₄NPF₆, 20 mM, in acetonitrile as electrolyte, and a silver wire and a platinum wire as the pseudoreference and counter electrode, respectively. b) Cyclic voltammetry of the SAM of La@C₈₂-S-Au acquired at different scan rates (from 0.1 V/s to 0.7 V/s). Two stable and reversible peaks at E^{1/2} 0.33 V and 0.69 V (at scan rate 0.3V/s). Inset: Plot of the current vs. scan rate at E = 0.37 V.

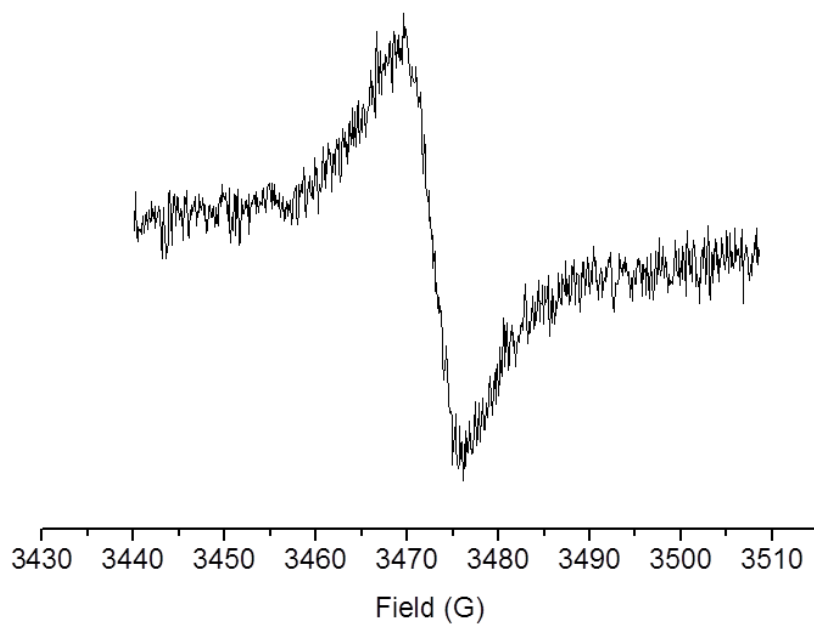


Figure S14. ESR spectrum of a drop casted film of La@C₈₂ derivative (**2b**) on gold showing a g factor of 2.0015 and a line width of 6.5 Gauss.