Electronic Supplementary Material (ESI) for ChemComm.
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# Supporting Information

## EXPERIMENTAL DETAILS

### General Instruments

High performance liquid chromatography (HPLC) was conducted on an LC-908 machine (Japan Analytical Industry Co., Ltd) using toluene as the mobile phase. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry were measured on a BIFLEX$^{TM}$ III spectrometer (Bruker, Germany) using 1,1,4,4-tetraphenyl-1,3-butadiene as matrix. Vis-NIR spectra were measured on a LAMBDA 750 UV/Vis/NIR Spectrophotometer (PerkinElmer, US) in $CS_2$. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were measured in 1,2-dichlorobenzene with 0.1 M ($n$-Bu)$_4$NPF$_6$ at a Pt working electrode on a CHI660E workstation (BAS CW-50). The scan rate of CV was 20 mV s$^{-1}$. Conditions of DPV: pulse amplitude = 50 mV; scan rate = 20 mV s$^{-1}$. X-ray diffraction measurements were performed at 90 K on a Bruker AXS machine equipped with an Apex II CCD. The multi-scan method was used for absorption corrections.

Calculations were conducted with the Gaussian 09 program package.[S1] Geometries were optimized at the B3LYP level [3-21G(d) at C atoms and SDD with ECP at Pr] [S2-4].

**Chemical functionalization of Pr@$C_{2v}$(9)-$C_{82}$**

A sealed Pyrex tub*e* containing 50 mL toluene solution of 5 mg Pr@$C_{82}$ and an excess amount (ca. 30-fold) of 2-adamantane-2,3-[3H]-diazirine (1) was degassed with the freeze-pump-thaw method. The mixture was photo-irradiated with an ultra-high pressure mercury-arc lamp (cutoff < 350 nm) at room temperature. The reaction was monitored with HPLC. Before irradiation, the starting material Pr@$C_{82}$ gave a strong peak at 16.5 min. After 10-min irradiation, new peaks appeared at 11.4 and 12.0 min, respectively, which are ascribed to the monoadducts 2 according to mass spectrometric results. The reaction was terminated when a small amount of bisadduct was formed after 40-min irradiation. Then the reaction mixture was concentrated and filtrated for subsequent HPLC separation. One-step HPLC separation gave rise to the two isomers of monoadducts 2 in 90% yield based on consumed Pr@$C_{82}$ (Figure S1). The relative yield of 2a and 2b is roughly 4:1.

Black crystals of 2a suitable for X-ray diffraction studies were grown from $CS_2$/hexane in a glass tube (*i.d.* = 7.0 mm) at 273K over two weeks. X-ray data were collected at 90 K on a D8 QUEST machine (Bruker Analytik, Germany) equipped with a PHOTON camera. The structure was solved with a direct method and was refined using SHLEX 97.[S5] CCDC 981979 contains the supplementary crystallographic data for 2a.

**References:**

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S3 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* 1988, **37**, 785-789.

S4 A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648-5652.

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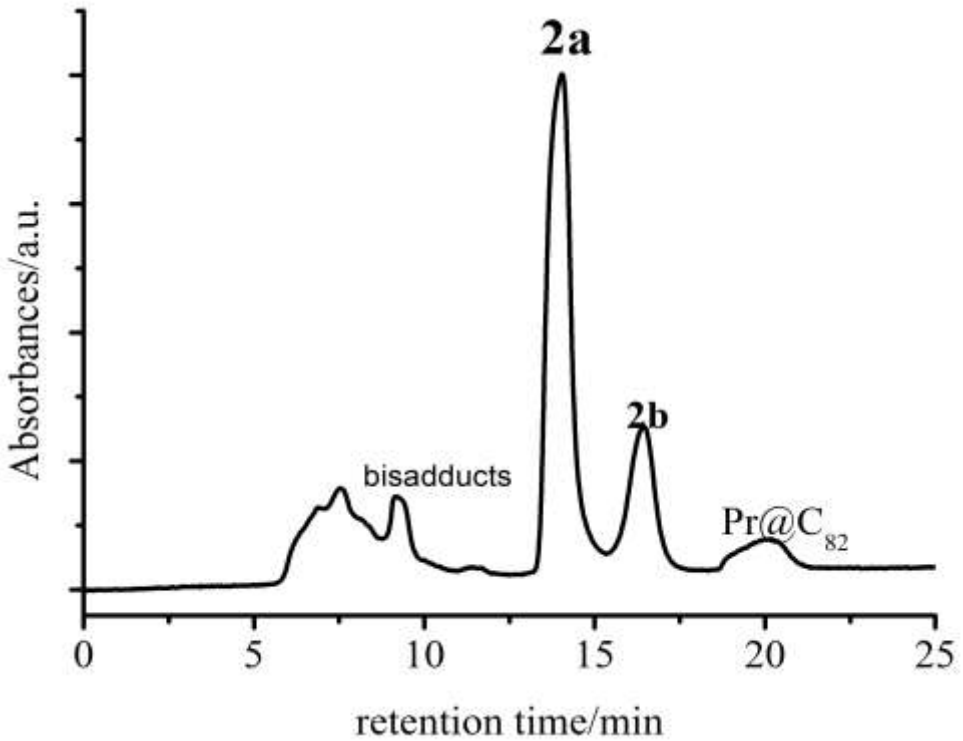


**Fig. S1** HPLC separation profile of the reaction mixture of $Pr@C_{82}$ and 1. Conditions: 5-PYE column ($\phi 20 \times 250$ mm); 10.0 mL/min toluene flow; room temperature; 330 nm detector wavelength.

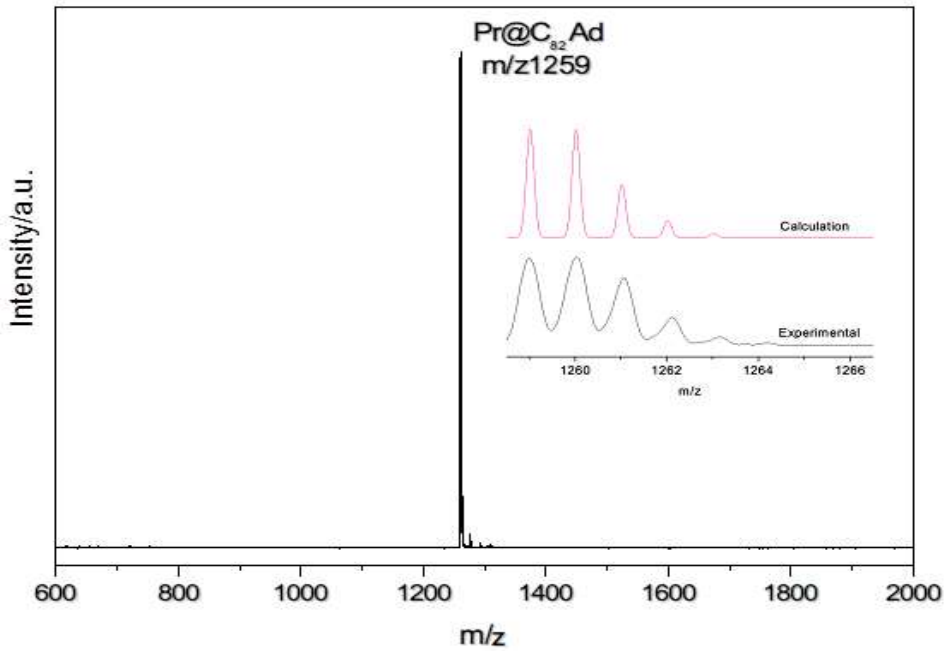


**Fig. S2** Mass spectrum of **2a** in a negative reflection mode.

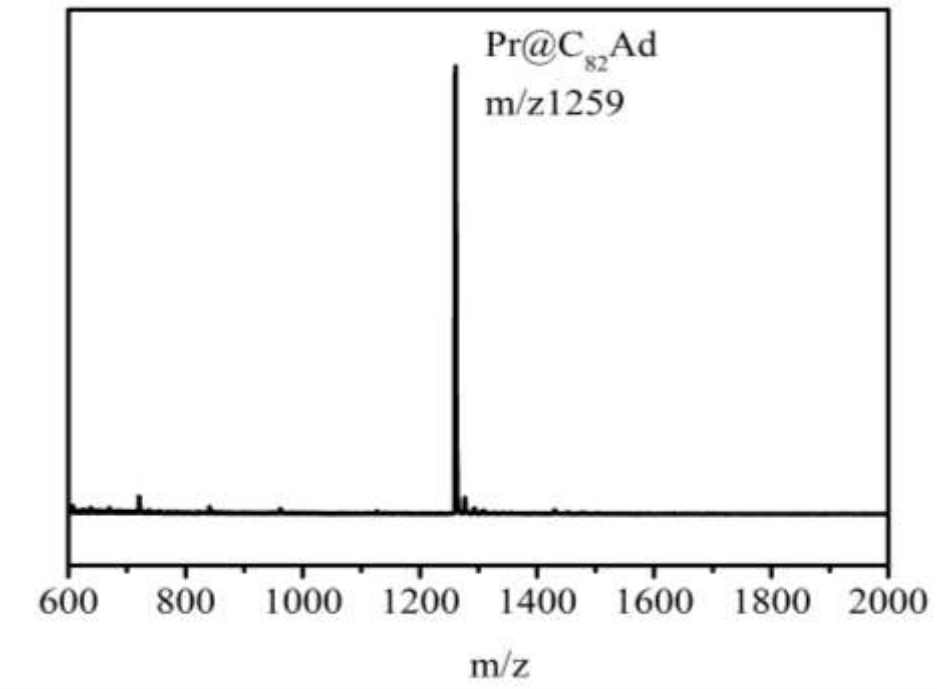


**Fig. S3** MALDI-TOF mass spectrum of **2b**.

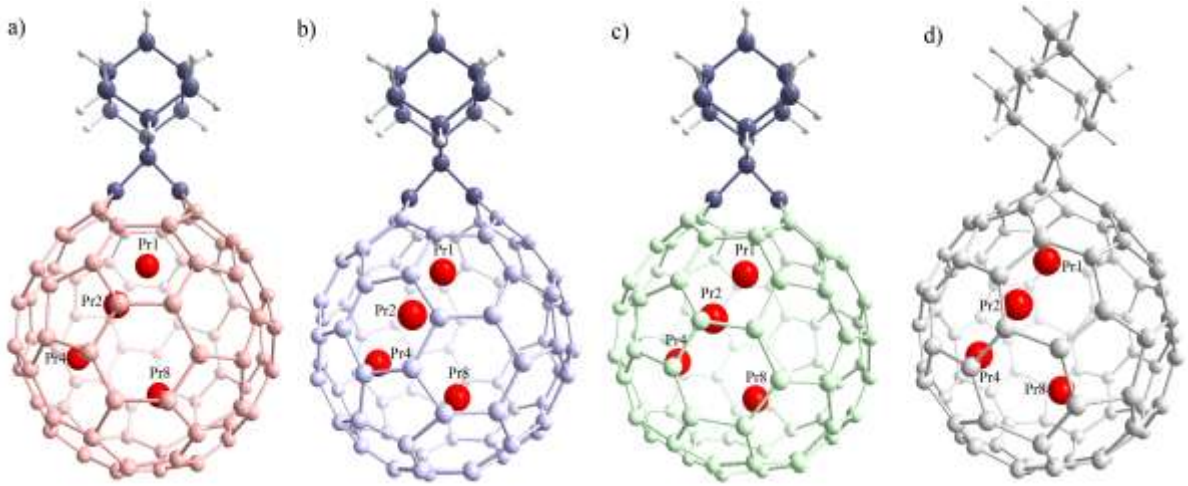


**Fig. S4** Drawings showing the disorders in the crystal structure of Pr@$C_{82}$Ad (graphs a, b, c use the same Ad group in same color and graph d uses the minor one).

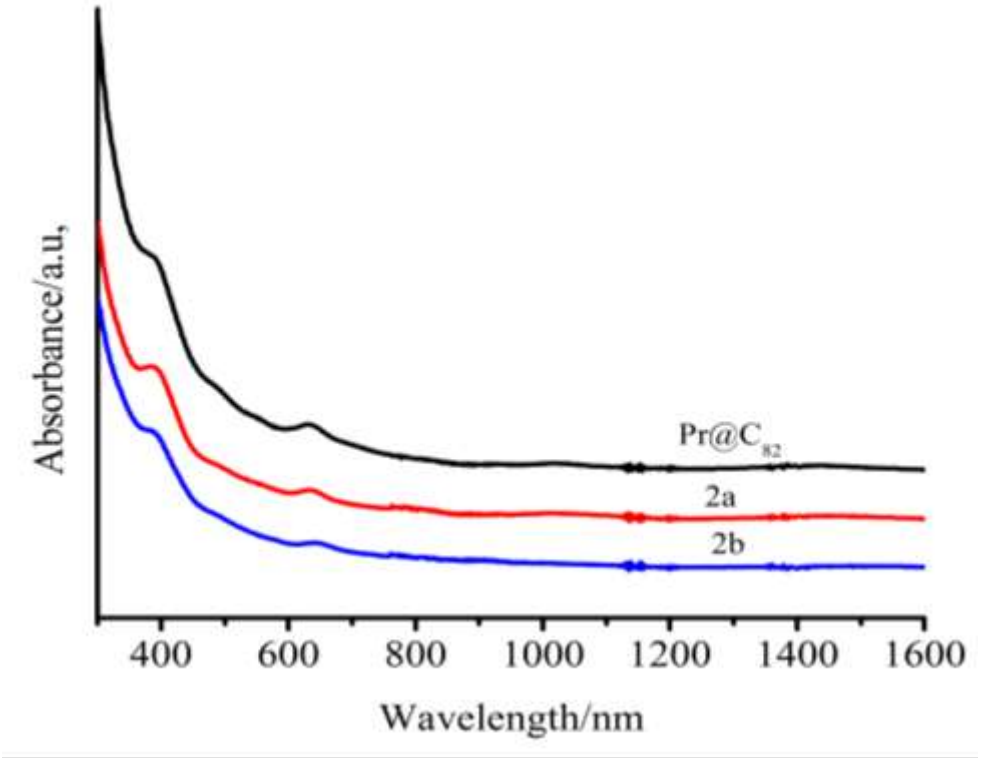


**Fig. S5** Vis-NIR spectra of Pr@$C_{2v}$(9)-$C_{82}$, **2a** and **2b**.

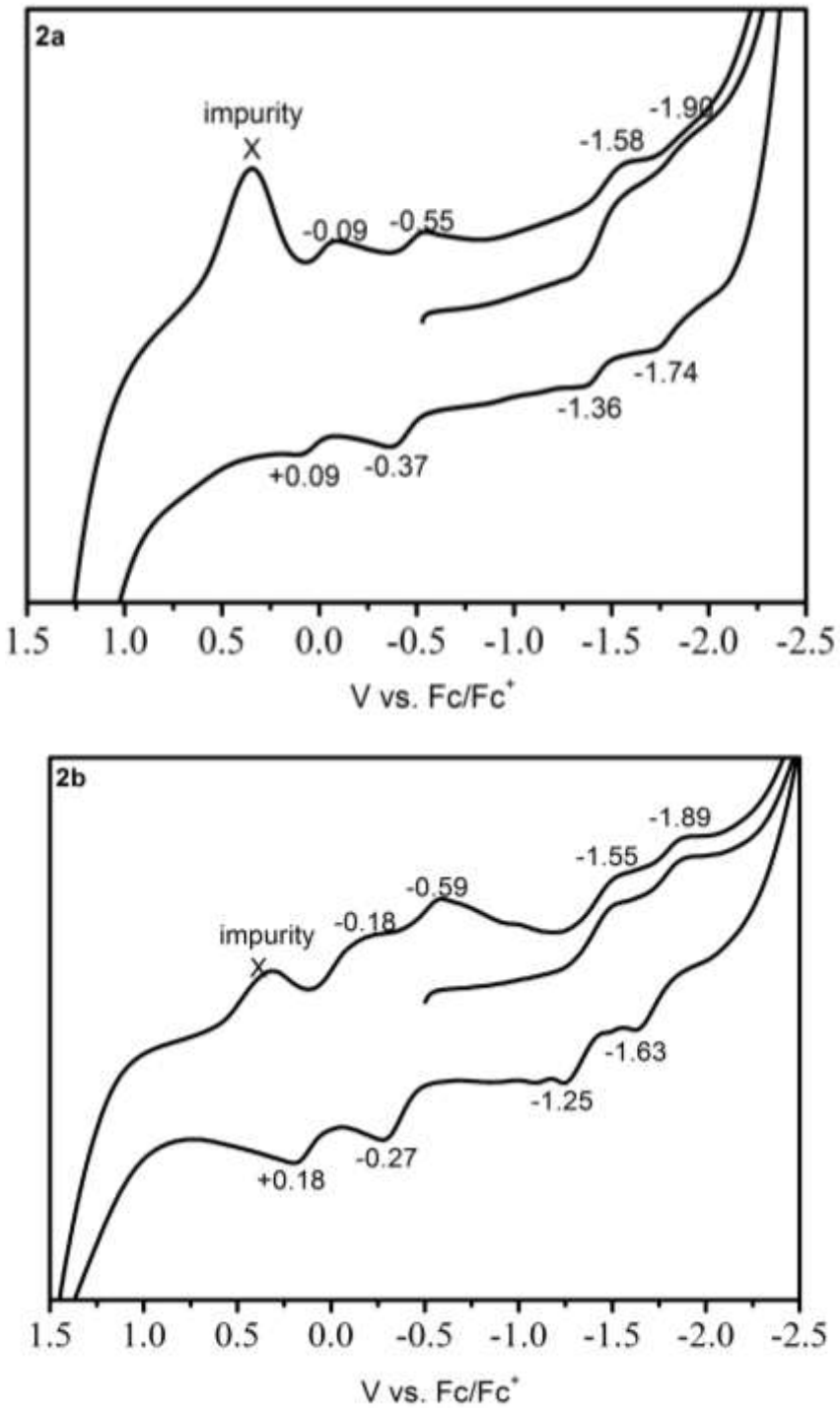


**Fig. S6** CV spectra of **2a** and **2b**.