Electronic Supplementary Information for

Strongest π-Metal Orbital Coupling in a Porphyrin/Gold Cluster System†

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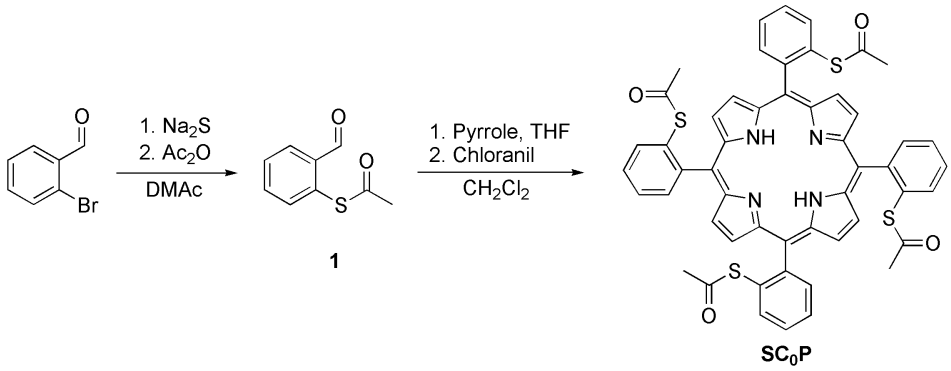
Synthesis of SC$_n$P and SC$_n$P–AuCs

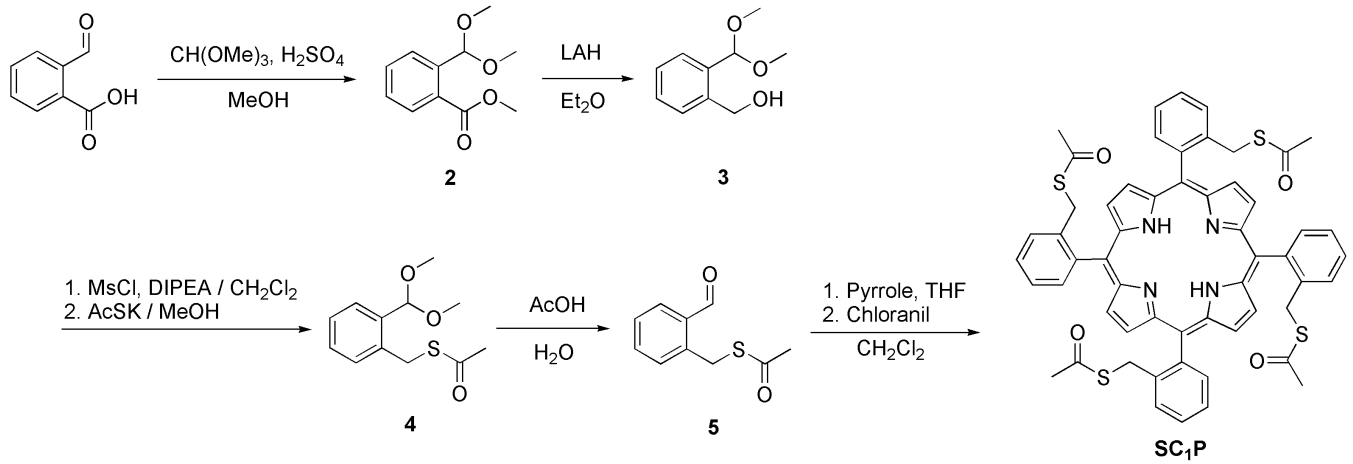
Materials: All materials were purchased from commercial suppliers and used as received.

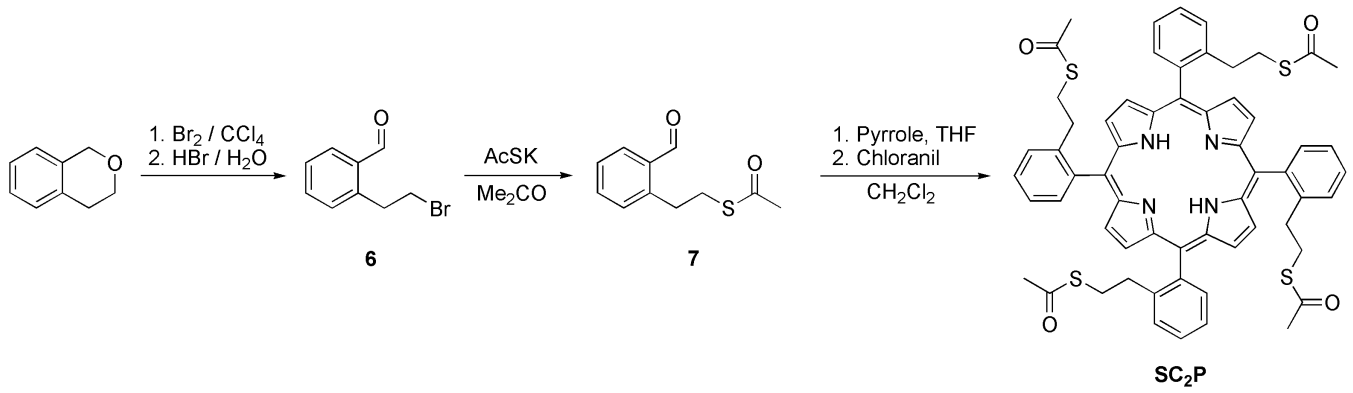
Instruments: ^{1}H and ^{13}C NMR spectra were recorded on a 200 MHz Varian Gemini 200 NMR spectrometer and a Bruker Avance III 600US Plus NMR system. Gel permeation chromatography high-performance liquid chromatography (GPC-HPLC) was carried out using a LC-908 (Japan Analytical Industry Co., Ltd.) with a JAIGEL-W253 column. GPC-HPLC chromatograms were recorded on a Shimadzu UV-3150. Matrix assisted laser desorption/ionization time-of-flight mass (MALDI-TOF MS) spectra were measured on a time-of-flight mass spectrometer (Applied Biosystems, Voyager-DE STR-H) operated with a N_2 laser (337 nm, 3 Hz, <100 μJ). Mass calibration in MALDI-TOF MS was carried out using a peptide calibration standard II (Bruker Co.). Gas chromatography mass spectrometry (GC-MS) data were recorded on a Shimadzu GCMS-QP5050. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were carried out using a PerkinElmer Optima 7300DV. UV-vis-NIR absorption spectra measurements were carried out using a Hitachi U-4100. Transmission electron microscope (TEM) images were obtained using a JEOL JEM-100. High-angle annular dark field scanning transmission electron microscope (HAADF-STEM) images were obtained using a Hitachi High-Technologies HD-2300C operating at 200 kV equipped with a spherical aberration corrector. The details of the femtosecond transient absorption spectrometer have been discussed elsewhere.[1,2] Briefly, the light source for the femtosecond pump-probe transient absorption measurements was a regenerative amplifier system consisting of a Ti:sapphire laser (800 nm wavelength, 130 fs fwhm pulse width, 0.8 mJ/pulse intensity, 1 kHz repetition; Spectra Physics, Hurricane) combined with an optical parametric amplifier (OPAs; Quantronix, TOPAS). For a pump pulse, the output of the OPA at a wavelength of 520 or 560 nm with an intensity of about 2 μJ per pulse at a 500-Hz modulation frequency was used. For a probe pulse, the white light continuum generated by focusing the fundamental beam (800 nm) onto a sapphire plate (2

mm thick) was used. The probe beam was focused at the center of the pump beam on the sample, and the transmitted probe beam was then detected using an InGaAs photodetector after passing through a monochromator (Acton Research, SpectraPro-150). The time resolution of the measurements was about 250 fs. All measurements were performed at 295 K.

Synthesis of porphyrin derivatives: The synthesis procedures for SC_0P and SC_1P were partially modified from previous reports.[3,4] SC_2P was synthesized as previously reported.[3]







2-Acetylthiobenzaldehyde (1)

$Na_2S \cdot 9H_2O$ (15.6 g, 65.0 mmol) in *N,N*-dimethylacetamide (DMAc, 500 mL) was stirred at 90 °C for 20 min. 2-Bromobenzaldehyde (6.25 mL, 53.5 mmol) was added to the solution and it was continuously stirred at 90 °C for 30 min. Acetic anhydride (7.62 mL, 81.1 mmol) was added while cooling in an ice-water bath and the mixture was stirred for 12 min to obtain a yellow solution. Saturated $NaHCO_3$(aq) was added to the solution and stirred for 10 min. The product was extracted with dichloromethane (DCM), dried with Na_2SO_4, and concentrated under reduced pressure. The product was dissolved in hexane and washed with water several times to remove the DMAc. The solution was dried with Na_2SO_4 and concentrated under reduced pressure. Purification by column chromatography (silica gel, hexane: ethyl acetate = 9:1) afforded **1** (4.96 g, 51%) as a pale yellow oil.

^{1}H NMR (200 MHz, $CDCl_3$, 298 K, TMS): δ=10.2 (s, 1H), 7.99 (d, *J*=8.0 Hz, 1H), 7.48-7.53 (m, 3H), 2.48 (s, 3H). MS (EI): *m/z* (%): 180 (6) (M^+), 137 (100), 138 (89), 109 (58), 104 (36).

Tetrakis-5*α*,10*α*,15*α*,20*α*-(2-acetylthiophenyl)porphyrin (SC_0P)

Trifluoroacetic acid (3.06 mL, 40.0 mmol) was added to the DCM solution (2 L) of **1** (3.60 g, 20.0 mmol) and pyrrole (1.39 mL, 20.0 mmol) under a N_2 atmosphere. After stirring for 1 h at room temperature (RT), chloranil (3.44 g, 14.0 mmol) was added and the mixture was refluxed for 20 min. After cooling to RT, $NaHCO_3$(aq) was added to terminate the reaction. The DCM phase was extracted, washed with water, filtered through Celite, and concentrated under reduced pressure. Purification by column chromatography (silica gel, DCM) afforded SC_0P (82.3 mg, 1.8%) as a purple solid.

^{1}H NMR (600 MHz, $CDCl_3$, 298 K, TMS): δ=8.57 (d, *J*=15 Hz, 4H), 8.17 (dd, *J*=7.2 Hz, *J*=1.2 Hz, 2H), 7.90 (dd, *J*=8.4 Hz, *J*=1.5 Hz, 2H), 7.86 (ddd, *J*=7.8 Hz, *J*=7.8 Hz, *J*=1.8 Hz, 2H), 7.76 (ddd, *J*=7.8 Hz, *J*=7.2 Hz, *J*=1.8 Hz, 2H), 1.69 (s, 6H), –2.69 (d, *J*=6 Hz, 1H). ^{13}C NMR (600 MHz, $CDCl_3$, 298 K, TMS): δ=192.8, 145.2, 135.7, 134.9, 131.7, 130.7 (br), 129.3, 127.8, 118.0, 29.8. MS (MALDI): *m/z* (%): 911.2 (M^+). Calculated mass 911.18.

2-Dimetoxymethyl methyl benzoate (2)

Sulfuric acid (405 μL, 7.60 mmol) was added to the dehydrated methanol solution (200 mL) of terephthalaldehydic acid (76.1 g, 507 mmol) and trimethyl orthoformate (150 mL, 1.37 mol) under a N_2 atmosphere, and then the mixture was refluxed for 1 day. The reaction was terminated by adding $NaHCO_3$(aq). The product was extracted with DCM, dried with Na_2SO_4, and concentrated under reduced pressure to obtain **2** (106 g, 99%) as a colorless oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ=7.80 (m, 1H), 7.42 (m, 3H), 6.07 (s, 1H), 3.91 (s, 3H), 3.38 (s, 6H). MS (EI): *m/z* (%): 109 (100), 165 (53), 80 (32), 110 (22), 81 (10).

2-Hydroxymethyl benzaldehyde dimethylacetal (3)

Lithium aluminum hydride (19.1 g, 504 mmol) was dissolved in dehydrated diethyl ether (400 mL) under a N_2 atmosphere. **2** (106 g, 504 mmol) was added dropwise while cooling in an ice-water bath and the mixture was refluxed for 4 h. After cooling in an ice-water bath, 20 mL water, 4 M NaOH(aq) (20 mL) and 60 mL water were, in turn, added dropwise. The mixture was stirred for 30 min at RT. The resulting precipitate was filtered through Celite and the filtrate was extracted with diethyl ether. The diethyl ether solution was washed with water, dried with Na_2SO_4, and concentrated under reduced pressure to obtain **3** (78.7 g, 79%) as a colorless oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ=7.49-7.55 (m, 1H), 7.30-7.41 (m, 3H), 5.51 (s, 1H), 4.71 (d, *J*=6.6 Hz, 2H), 3.37 (s, 6H), 3.19 (t, *J*=6.6 Hz, 1H). MS (EI): *m/z* (%): 119 (100), 91 (79), 149 (26), 89 (14).

2-Acethylthiomethyl benzaldehyde dimethylacetal (4)

Methanesulfonyl chloride (39.2 mL, 506 mmol) was added dropwise under a N_2 atmosphere to the dehydrated DCM solution (200 mL) of *N,N'*-diisopropylethylamine (90.0 mL, 506 mmol) and **3** (78.7 g, 397 mmol) while cooling in an ice-water bath. The mixture was stirred at 0 °C for 2 h and then continuously at RT for 1 h. The mixture was washed with water, dried with Na_2SO_4, and concentrated under reduced pressure to obtain a yellow oil. Potassium thioacetate (48.2 g, 422 mmol) was slowly

added to the methanol solution to dissolve the obtained yellow oil while cooling in an ice-water bath, and then the mixture was stirred at RT for 3 h. The product was extracted with DCM, washed with water, dried with Na_2SO_4 and concentrated under reduced pressure to obtain **4** (98.0 g, 96%) as a yellow oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ=7.47-7.54 (m, 1H), 7.20-7.40 (m, 3H), 5.47 (s, 1H), 4.28 (s, 2H), 3.33 (s, 6H), 2.34 (s, 3H). MS (EI): *m/z* (%): 135 (100), 165 (89), 134 (61), 91 (40), 119 (24), 105 (26).

2-Acethylthiomethylbenzaldehyde (5)

Acetic acid (150 mL) was added to the aqueous solution (80 mL) of **4** (98.0 g, 382 mmol) and then the mixture was stirred at RT for 2 h. $NaHCO_3$(aq) was added to terminate the reaction. The product was extracted with DCM, dried with Na_2SO_4, and concentrated under reduced pressure. Purification by column chromatography (silica gel, hexane: ethyl acetate = 4:1) afforded **5** (72.1 g, 97%) as a yellow oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ=10.2 (s, 1H), 7.82-7.87 (m, 1H), 7.42-7.60 (m, 3H), 4.55 (s, 2H), 2.35 (s, 3H). MS (EI): *m/z* (%): 151 (100), 134 (75), 91 (69), 118 (53), 90 (41).

Tetrakis-5*α*,10*α*,15*α*,20*α*-(2-acetylthiometylphenyl)porphyrin (SC_1P)

Trifluoroacetic acid (3.06 mL, 40.0 mmol) was added to the DCM solution (2 L) of **5** (3.89 g, 20.0 mmol) and pyrrole (1.39 mL, 20.0 mmol) under a N_2 atmosphere. After stirring for 1 h at RT, chloranil (3.44 g, 14.0 mmol) was added and then the mixture was refluxed for 20 min. After cooling to RT, $NaHCO_3$(aq) was added to terminate the reaction. The DCM phase was extracted, washed with water, filtered through Celite, and concentrated under reduced pressure. Purification by column chromatography (silica gel, DCM) afforded SC_1P (105 mg, 2%) as a purple solid.

^{1}H NMR (200 MHz, $CDCl_3$): δ=8.64 (s, 4H), 7.99 (dd, *J*=7.8 Hz, *J*=1.2 Hz, 2H), 7.70-7.86 (m, 4H), 7.59 (dt, *J*=7.2 Hz, *J*=1.6 Hz, 2H), 3.92 (s, 4H), 2.02 (s, 6H), –2.67 (s, 1H). MS (ESI): *m/z*: 967.2 ($M+H^+$).

2- (2-Bromoethyl)benzaldehyde (6)

Isochroman (25.0 g, 186 mmol) was added to tetrachloromethane (100 mL) under a N_2 atmosphere

and the solution was cooled in an ice-water bath. Bromine (30.0 g, 188 mmol) was added dropwise to the solution and the solution was refluxed for 90 min. The solution was cooled and concentrated under reduced pressure to obtain a yellow oil. Hydrobromic acid (56.8 g, 330 mmol) was added to the obtained yellow oil and the solution was refluxed for 20 min under a N_2 atmosphere. After cooling to room temperature the reaction was terminated by adding $NaHCO_3$(aq). The product was extracted with DCM, washed with water, dried with Na_2SO_4, and concentrated under reduced pressure. Purification by column chromatography (silica gel, hexane: ethylacetate = 3:1) afforded **6** (31.3g, 78%).

^{1}H NMR (200 MHz, $CDCl_3$): δ=10.1 (s, 1H), 7.31-7.84 (m, 4H), 3.56-3.64 (m, 4H). MS (EI): *m/z* (%): 133 (100), 105 (17), 91 (14), 103 (12), 134 (10).

2-Acethylthioethylbenzaldehyde (7)

Potassium thioacetate (16.8 g, 147 mmol) was slowly added to the acetone solution of **6** (31.3 g, 147 mmol) while cooling in an ice-water bath and the mixture was stirred at RT for 3 h. The product was extracted with DCM, washed with water, dried with Na_2SO_4, and concentrated under reduced pressure to afford **7** (27.9 g, 91%).

^{1}H NMR (200 MHz, $CDCl_3$): δ=10.2 (s, 1H), 7.34-7.81 (m, 4H), 3.10-3.29 (m, 4H), 2.32 (s, 3H). MS (EI): *m/z* (%): 132 (100), 133 (94), 148 (84), 147 (59), 91 (47), 119 (42), 104 (38), 149 (30), 115 (29), 103 (28).

Tetrakis-5*α*,10*α*,15*α*,20*α*-(2-acetylthioetylphenyl)porphyrin (SC_2P)

Trifluoroacetic acid (3.06 mL, 40.0 mmol) was added to a DCM solution (2 L) of **7** (4.17 g, 20.0 mmol) and pyrrole (1.39 mL, 20.0 mmol) under a N_2 atmosphere. After stirring for 1 h at RT, chloranil (3.44 g, 14.0 mmol) was added and the mixture was refluxed for 20 min. After cooling to RT, $NaHCO_3$(aq) was added to terminate the reaction. The DCM phase was extracted, washed with water, filtered through Celite, and concentrated under reduced pressure. Purification by column chromatography (silica gel, DCM) afforded SC_2P (104 mg, 2%) as a purple solid.

^{1}H NMR (200 MHz, $CDCl_3$): δ=8.66 (s, 4H), 7.95 (dd, J=7.8 Hz, J=1.2 Hz, 2H), 7.75-7.78 (m, 4H), 7.55 (dt, J=7.2 Hz, J=1.6 Hz, 2H), 2.71 (m, 8H), 2.02 (s, 6H), –2.69 (s, 1H).

Synthesis of SC_0P–AuCs: $HAuCl_4$•$4H_2O$ (20.6 mg, 50 μmol) was dissolved in 10 mL of Nanopure water and tetraoctylammonium bromide (30.1 mg, 55 μmol) in 50 mL of DCM, and these were mixed in a 200 mL conical flask. The solution was stirred vigorously with a magnetic stir bar to facilitate the phase transfer of the Au^{III} salt into the DCM phase. After approximately 15 min, phase transfer was complete and the clear aqueous phase was removed. SC_0P (9.1 mg, 10 μmol) in DCM (5 mL) and methanol (50 mL) was added to the DCM solution of Au^{III}. The mixed solution was cooled to –98 °C in a bath containing methanol and liquid N_2. On reaching –98 °C, a methanol solution of $NaBH_4$ (18.9 mg, 500 μmol) was quickly added to the solution. The reaction was allowed to proceed for 15 min. After 200 mL Nanopure water was added to remove byproducts and methanol, the solution was slowly stirred for 20 min. The DCM phase was collected and dried by Na_2SO_4. After 3 mL *N*,*N*-dimethylformamide (DMF) was added, the only DCM was evaporated under reduced pressure. The obtained SC_0P-AuCs in DMF was purified by GPC-HPLC. The purified SC_0P-AuCs was stored in DMF.

Synthesis of SC_1P– and SC_2P–AuCs: SC_1P– and SC_2P–AuCs were synthesized as previously reported.[3] $HAuCl_4$•$4H_2O$ (3.2 μmol) was dissolved in 1 mL of Nanopure water and tetraoctylammonium bromide (3.5 μmol) was dissolved in 1 mL of DCM, and these were mixed in a glass vial. The solution was stirred vigorously with a magnetic stir bar to facilitate the phase transfer of the Au^{III} salt into the DCM phase. After approximately 15 min, phase transfer was complete and the clear aqueous phase was removed. SC_nP (n = 1 and 2) (1.6 μmol) in DCM (1 mL) and methanol (3 mL) was added to the DCM solution of Au^{III}. The mixed solution was cooled to –98 °C in a bath containing methanol and liquid N_2 over 30 min with magnetic stirring. On reaching –98 °C, a methanol solution of $NaBH_4$ (32 μmol, 10 equiv. of the moles of Au) was quickly added to the solution. The reaction was allowed to proceed for 4 h. A brown powder precipitated in the vial and was collected by filtration. The brown powder was extracted with

DCM. The obtained SC_nP-AuCs were dispersed in DMF and purified by gel permeation chromatography (JAIGEL-W253). The purified SC_nP-AuCs was stored in DMF.

Computational method

All the density functional theory calculations were performed with a plane wave basis set and ultrasoft pseudopotentials[5] as implemented in the STATE[6] code. The Perdew-Ernzerhof-Burke[7] generalized gradient approximation was used for the exchange correlation functional. The plane wave cutoffs for the wave functions and the augmentation charge were 25 and 225 Ry, respectively, and the Γ-point was used to sample the Brillouin zone. A SC_0P molecule was placed in a repeat tetragonal unit cell with edges of 2.117×2.117×1.323 nm. During the structural optimization the atoms were allowed to relax until the forces acting on them were less than 0.8 nN.

GPC chromatogram of SC_nP–AuCs

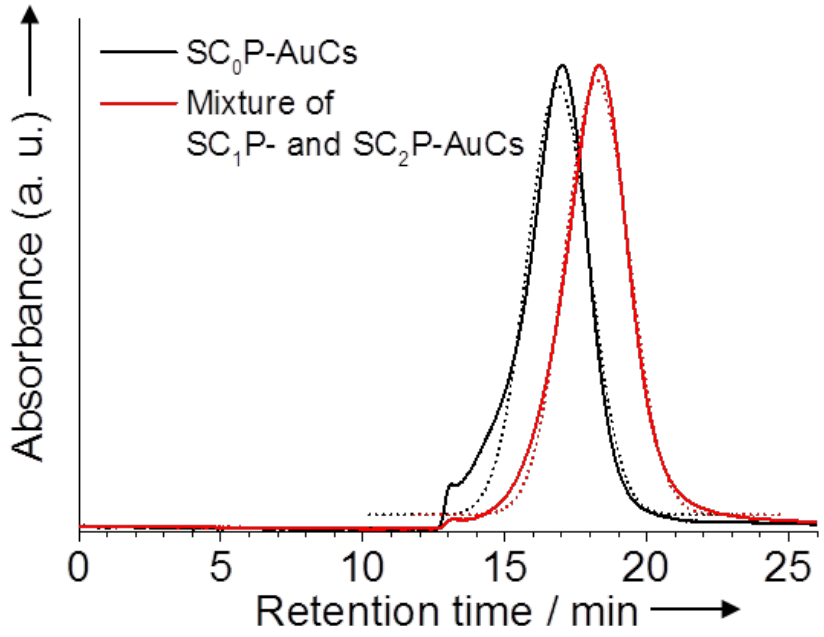


Figure S1. GPC chromatograms of SC_0P–AuCs and a mixture of SC_1P– and SC_2P–AuCs. Solid lines: experimental data. Broken lines: Gauss fitting.

Figure S1 shows GPC chromatograms of SC_0P–AuCs and a mixture of SC_1P– and SC_2P–AuCs. The retention times of SC_1P– and SC_2P–AuCs were similar. Conversely, SC_0P–AuCs showed a peak at 17.0 min, which is 1.3 min faster than the peak of the mixture (18.3 min), indicating that the SC_0P–AuCs has a larger volume than SC_1P– or SC_2P–AuCs. The peak shapes of the SC_nP–AuCs showed a Gaussian distribution, indicating that the SC_nP–AuCs consist of single components.

Decay profiles for free SC_0P and SC_0P–AuCs

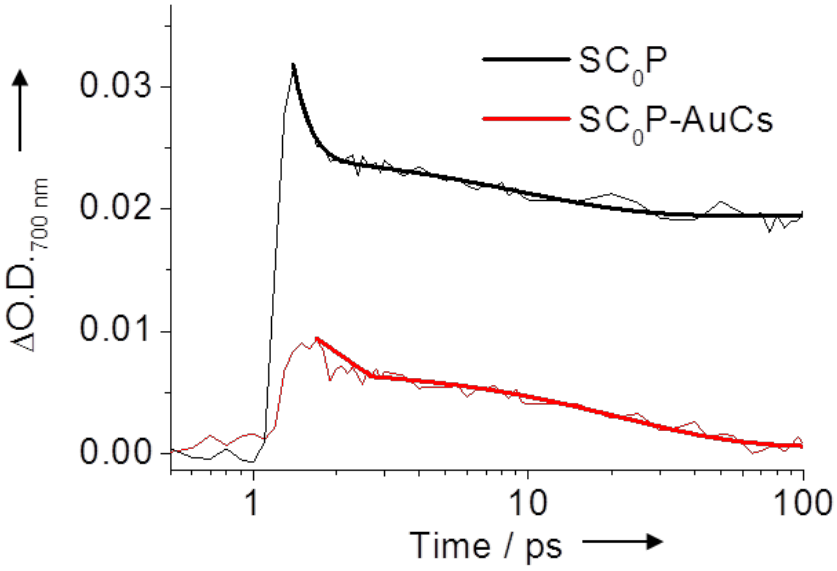


Figure S2. Decay profiles of free SC_0P and SC_0P–AuCs in DMF at 700 nm after laser excitation at 520 nm.

Decay profiles of excited free SC_0P and SC_0P–AuCs at 700 nm were fitted by a double exponential decay function. The decay profile of free SC_0P showed a fast decay component (< 300 fs) and this is assigned to a vibrational relaxation from the vibrational-excited state, and a long-lived component, which is assigned to the deactivation of the S_1 state. Conversely, the decay profile for SC_0P–AuCs exhibited a fast and slow component, estimated to be 700 fs and 32 ps, respectively. The fast and slow components likely correspond to the formation of an exciplex and charge separation, respectively.

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