Regioselective Thiocyanation of Corroles and the synthesis of Gold nanoparticle–Corrole assemblies

Kasturi Sahu, a Sruti Mondal, a Bratati Patra, a Tanmoy Pain, a Sajal Kumar Patra, a Carsten Dosche* b, and Sanjib Kar* a

a School of Chemical Sciences, National Institute of Science Education and Research (NISER), Bhubaneswar, Khordha, 752050, India and Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai, 400 094, India

b University of Oldenburg, Institute of Chemistry, Carl-von-Ossietzky-St. 9-11, 26129 Oldenburg, Germany

E-mail: sanjib@niser.ac.in; carsten.dosche@uol.de
Experimental Section

Materials

The precursor’s pyrrole, HAuCl₄, p-chloranil, and aldehydes were purchased from Aldrich, USA. NH₄SCN (>98.5% purity), Carbon disulphide was purchased from Merck pvt. ltd chemicals. Other chemicals were of reagent grade. Hexane and CH₂Cl₂ were distilled from KOH and CaH₂ respectively. For spectroscopy studies, HPLC grade solvents were used. 5,10,15-triphenylcorrole was prepared by following the previous literatures.¹

Physical Measurements

UV–Vis spectral studies were performed on a Perkin–Elmer LAMBDA-750 spectrophotometer. Emission spectral studies were performed on a Perkin Elmer, LS 55 spectrophotometer using optical cell of 1 cm path length. Time resolved fluorescence measurements were carried out using a time-correlated single photon counting (TCSPC) spectrometer (Edinburgh Instruments, Life Spec II). The elemental analyses were carried out with a Perkin–Elmer 240C elemental analyzer. FT–IR spectra were recorded on a Perkin–Elmer spectrophotometer with samples prepared as KBr pellets. The NMR measurements were carried out using a Bruker 400 MHz NMR spectrometer. Chemical shifts are expressed in parts per million (ppm) relative to residual chloroform (δ= 7.26). Electrospray mass spectra were recorded on a Bruker Micro TOF─QII mass spectrometer. Transmission electron microscope (TEM) images for size and size distribution were obtained by using a JEOL JEM-F200 (operating at 200 kV) equipped with an energy dispersive spectrometer (EDS). TEM images for the samples were obtained by using a One View camera (Gatan, Pleasanton, CA). XPS spectra were measured using an Escalab 250 Xi spectrometer (Thermo Fisher, East Grinstead, UK) equipped with a monochromatized Al Kα source (1486.6 eV) and external charge compensation. Survey spectra were measured with a band pass of 100 eV, detail spectra for N 1s, C 1s, O 1s, S 2p and Au 4f with a band pass of 10 eV. Data acquisition and evaluation were done using the software Avantage (Version 5.982, Thermo Fisher).
Crystal Structure Determination

Single crystals of 1 were grown by slow diffusion of a solution of the 1 in dichloromethane into hexane, followed by slow evaporation under atmospheric conditions. The crystal data of 1 were collected on a Rigaku Oxford diffractometer at 293 K. Selected data collection parameters and other crystallographic results are summarized in Table S1. All data were corrected for Lorentz polarization and absorption effects. The program package SHELXTL\(^2\) was used for structure solution and full matrix least squares refinement on F\(^2\). Hydrogen atoms were included in the refinement using the riding model. Contributions of H atoms for the water molecules were included but were not fixed. Disordered solvent molecules were taken out using SQUEEZE command in PLATON.\(^3\)

CCDC 1901425 contain the supplementary crystallographic data for 1. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Syntheses

Synthesis of 3,17-bis(thiocyanato)-5,10,15-triphenylcorrole, 1:

25 mg (0.0475mmol) of 5,10,15-triphenylcorrole was dissolved in 20ml of carbon disulfide, and then excess amount of NH\(_4\)SCN (approx. 2gm) was added to it. The reaction mixture was stirred for 5 mins at RT and then 20ml of pyridine was added to it and the resulting solution was refluxed for 3 hours. The residual solvent was evaporated to dryness and the crude product was dissolved in dichloromethane, white color precipitated was separated through filtration and the green color solution was kept under dark for 24 hours. The crude product was purified by using a column chromatography through silica gel (100-200 mesh). The desired fraction was eluted by using a mixture of 40% DCM and 60% hexane.

For 3,17-bis(thiocyanato)-5,10,15-triphenylcorrole, 1:

Yield: 40% (12 mg). Anal. Calcd (found) for C\(_{39}\)H\(_{24}\)N\(_6\)S\(_2\) (1): C, 73.10 (73.26); H, 3.78 (3.87); N, 13.12 (13.23); \(\lambda_{\text{max/nm}}\) (\(\varepsilon/\text{M}^{-1}\text{cm}^{-1}\)) in CH\(_2\)Cl\(_2\): 419 (103000), 574 (18000), 595 (17500), 656 (26000). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.88 (s, 2H, H-\(\beta\)), 8.61 (s, 2H, H-\(\beta\)), 8.43 (s, 2H, H-\(\beta\)), 8.08 (s, 6H, Ar-H), 7.78 (m, 9H, Ar-H), -1.38 (s, 3H). 1 displayed strong fluorescence at 688 nm in DCM. The electrospray mass spectrum in methanol showed peaks centred at \(m/z = 641.145\) corresponding to [1+H]\(^+\) (641.15 calcld for C\(_{39}\)H\(_{25}\)N\(_6\)S\(_2\)).
Preparation of 1 coated gold nanoparticles (1-Au NPs):

$10^{-3}$ M HAuCl$_4$ stock solution was prepared by dissolving 3.39 mg of HAuCl$_4$, 3H$_2$O in 10ml of DMF. Equimolar concentration of 3,17-bis(thiocyanato)$\cdot$5,10,15-triphenylcorrole solution was prepared by dissolving 6.40 mg of corrole in 10 ml of DMF. $10^{-2}$ M NaBH$_4$ stock solution was prepared in DMF. Initially a mixture of 0.5 ml corrole solution ($10^{-3}$ M) and 4.475 ml of HAuCl$_4$ ($10^{-3}$ M) solution was mixed together and stirred for 30 seconds. After that 2 ml NaBH$_4$ ($10^{-2}$ M) solution was added to the mixture and then stirred for another 2 hour 45 minutes. The color of the solution gradually changes from green to brown to red. After that the solution was centrifuged (10,000 rpm, RT for 20 minutes) and the obtained 1 coated Au-Nano-particles was washed with water for two times and then it was dispersed in water. For TEM measurements, copper grids pre-coated with carbon film, 300 mesh was used. The samples were prepared by using drop casting method.

For 1-Au NP:

Anal. Calcd (found) for $\{\text{Au}_{2997}(\text{C}_{37}\text{H}_{24}\text{N}_4\text{S}_2)_{200}\}$(1-Au NP): C, 12.54 (24.333); H, 0.68 (4.70); N, 1.58 (5.889), S, 1.81 (0.983). It is assumed that there are 2650±1450 Au atoms for each nanoparticle (Au nanoparticle having size of $\sim$4.4±0.8 nm). Thus the number 2997 (Au atoms) is purely an approximation to fit the data.

Sample Preparation for FT-IR measurement:

$10^{-3}$ M HAuCl$_4$ stock solution was prepared by dissolving 3.39 mg of HAuCl$_4$, 3H$_2$O in 10ml of DMF. Equimolar concentration of 3,17-bis(thiocyanato)$\cdot$5,10,15-triphenylcorrole solution was prepared by dissolving 6.40 mg of corrole in 10 ml of DMF. $10^{-2}$ M NaBH$_4$ stock solution was prepared in DMF. Initially a mixture of 10 ml corrole solution and 30 ml of NaBH$_4$ solution was mixed together and sonicated for 30mins. After that 10 ml HAuCl$_4$ solution was added to the prefixed mixture and the sonication was continued for another one hour. The color of the solution gradually changes from green to brown to red. After red color appears it was sonicated for another 2 hours. Then the mixture was stirred for another 12 hours. After that the solution was centrifuged (10,000 rpm, RT for 10 minutes) and the obtained 1 coated Au-Nano-particles were washed with water for two times and then it was dispersed in ethanol. The solution was evaporated to dryness and the FTIR spectra was recorded on a KBr pellet.
Notes and references

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2. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, 64, 112-122.
3. P. Van der Sluis and A. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, 46, 194-201.
4. A. J. Shaikh, F. Rabbani, T. A. Sherazi, Z. Iqbal, S. Mir and S. A. Shahzad, *J. Phys. Chem. A*, 2015, 119, 1108-1116
**Table S1**  Crystallographic data for 1.

**Table S2**  UV–Vis. Data.

**Fig. S1**  (a) Electronic absorption spectrum of 1 in dichloromethane.

**Fig. S1**  (b) Electronic absorption spectrum of 1 powder.

**Fig. S2**  Electronic emission spectrum (excited at the Soret band) of 1 in CH₂Cl₂.

**Fig. S3**  FT-IR spectrum of 1(−−−) and Gold nanoparticle–Corrole assemblies (−−−) as KBr pellet.

**Fig. S4**  ¹H NMR spectrum of 1 in CDCl₃.

**Fig. S5**  ESI-MS spectrum of 1 in CH₃CN shows the measured spectrum with isotopic distribution pattern.

**Fig. S6**  Electronic absorption spectrum for 1-Au NP.

**Fig. S7**  TEM image of the nanoparticles.

**Fig. S8**  TEM image of the nanoparticles.

**Fig. S9**  TEM image of the nanoparticles.

**Fig. S10**  EDS spectrum of 1-Au NP shows the presence of the entire constituent elements: Au, N, and S.
### Table S1  Crystallographic Data for 1.

| Property                        | Value                  |
|--------------------------------|------------------------|
| compound code                  | 1                      |
| molecular formula              | C$_{39}$H$_{24}$N$_{6}$S$_{2}$ |
| Fw                             | 641.47                 |
| Radiation                      | Cu Kα                  |
| crystal symmetry               | Triclinic              |
| space group                    | P-1                    |
| a(Å)                           | 8.6895 (2)             |
| b(Å)                           | 13.6651 (4)            |
| c(Å)                           | 13.7221 (3)            |
| α(deg)                         | 97.560                 |
| β(deg)                         | 104.489                |
| γ(deg)                         | 96.725                 |
| V(Å$^3$)                       | 1544.64(7)             |
| Z                              | 2                      |
| μ (mm$^{-1}$)                  | 1.878                  |
| T(K)                           | 298                    |
| $D_{\text{calc}}$ (g cm$^{-3}$) | 1.380                  |
| 2θ range (deg)                | 3.303 to 66.997        |
| e data ($R_{\text{int}}$)     | 4275 (0.0639)          |
| R1 ($I>2\sigma(I)$)           | 0.0647                 |
| WR2 (all data)                | 0.1813                 |
| GOF                            | 1.077                  |
| Δρ$_{\text{max}}$, Δρ$_{\text{min}}$ (e Å$^{-3}$) | 0.33, −0.41 |
Table S2  UV–Vis. data in dichloromethane

| Compound | UV–vis. Data                      |
|----------|----------------------------------|
|          | \( \lambda_{\text{max}} / \text{nm} \ (\varepsilon / \text{M}^{-1}\text{cm}^{-1}) \) |
| 1        | 419 (103000), 574 (18000), 595 (17500), 656 (26000) |
**Fig. S1**  
(a) Electronic absorption spectrum of 1 in dichloromethane.

**Fig. S1**  
(b) Electronic absorption spectrum of 1 powder.
Fig. S2  Electronic emission spectrum (excited at the Soret band) of 1 in CH₂Cl₂.
Fig. S3 FT-IR spectrum of 1(—) and Gold nanoparticle–Corrole assemblies (—) as KBr pellet.
Fig. S4  $^1$H NMR spectrum of 3,17-bis(thiocyanato)−5,10,15-triphenylcorrole, 1 in CDCl$_3$. 
Fig. S5  ESI-MS spectrum of 3,17-bis(thiocyanato)−5,10,15-triphenylcorrole, 1 in CH$_3$CN shows (a) the measured spectrum and (b) with isotopic distribution pattern.
Fig. S6  
Electronic absorption spectrum for 1-Au NP
Fig. S7  TEM image of the nanoparticles
Fig. S8  TEM image of the nanoparticles
Fig. S9  TEM image of the nanoparticles
**Fig. S10**  EDS spectrum of **1-Au NP** shows the presence of the entire constituent elements: Au, N, and S.