

Supplementary Information

Photoisomerization of Azobenzene Derivatives Confined in Gold Nanoparticle Aggregates

Jun Hee Yoon and Sangwoon Yoon*

Department of Chemistry, Institute of Nanosensor and Biotechnology, Dankook University

126 Jukjeon-dong, Suji-gu, Yongin

Gyeonggi 448-701

KOREA

Phone: +82-31-8005-3152

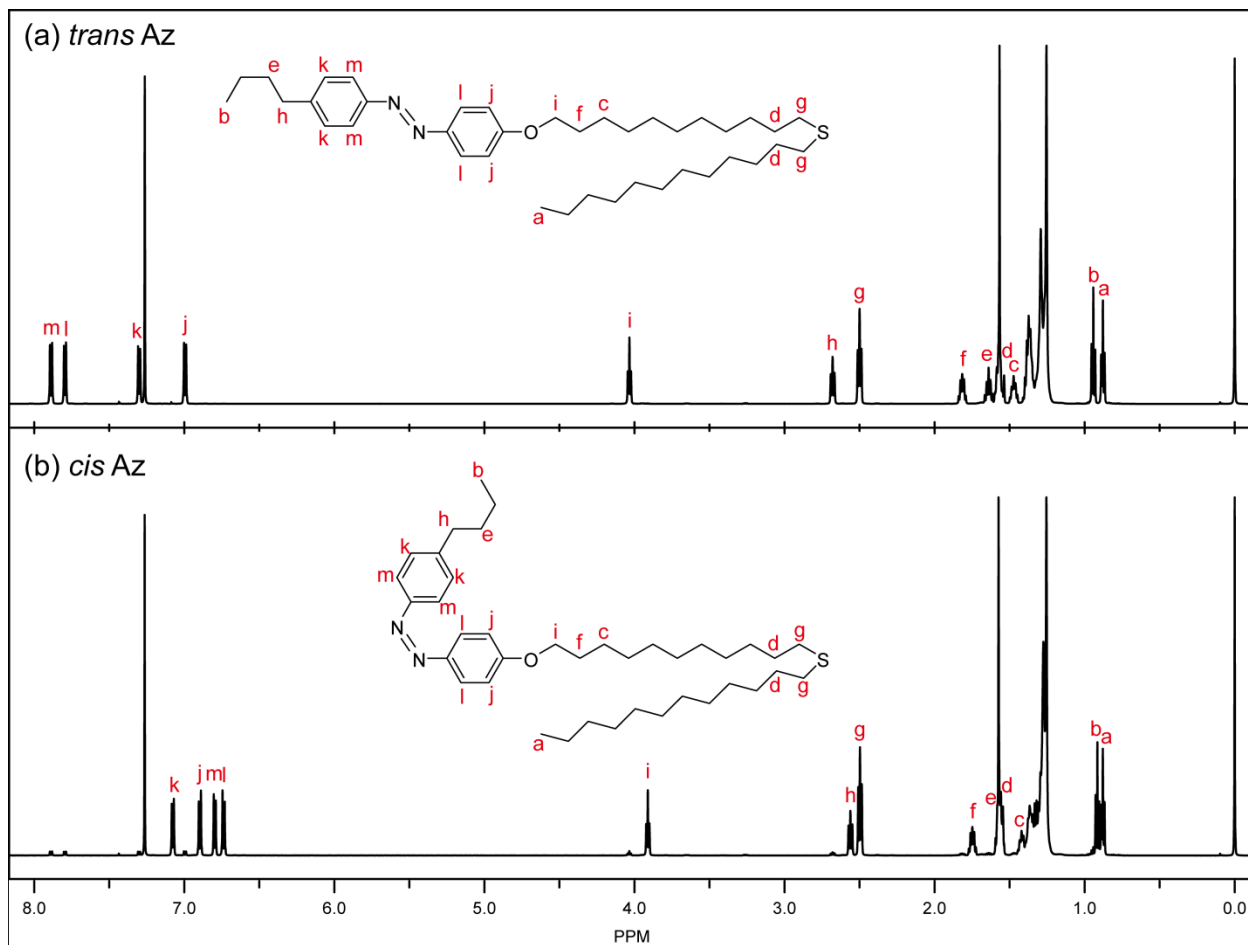
Fax: +82-31-8005-3148

E-mail: sangwoon@dankook.ac.kr

1. Characterization of Synthesized Az

1.1 NMR

The final product from the synthesis procedure described in the manuscript was characterized using NMR (Bruker, Avance 600, 600 MHz, 14.1 T). Fig. S1a presents the NMR spectrum of the product assigned to *trans* Az. To ensure that the final product was predominantly the *trans* isomer, the NMR spectrum of the product was compared to that of the irradiated product. For the latter, we dissolved the product in CDCl₃ and then irradiated the sample at 365 nm for 30 min at 3 mW/cm². Fig. S1b presents the NMR spectrum of the irradiated product, taken in the dark to minimize any backisomerization during the measurements. Fig. S1 shows that the peaks assigned to the protons nearest to the isomerization centre (marked m and l) dramatically shift upfield upon isomerization. Other protons near the N=N bond labelled k and j are also less deshielded by the isomerization. These spectral changes are consistent with previous observations for other types of azobenzene derivatives.¹ The marked difference between the NMR spectra confirms that the final product of the synthesis was *trans* Az.



(a) ^1H NMR (600 MHz, CDCl_3): δ 7.89 (d, 2H, $j = 8.9$ Hz), 7.79 (d, 2H, $j = 8.3$ Hz), 7.30 (d, 2H, $j = 8.3$ Hz), 6.99 (d, 2H, $j = 8.9$ Hz), 4.03 (t, 2H, $j = 6.6$ Hz), 2.68 (t, 2H, $j = 7.7$ Hz), 2.50 (t, 4H, $j = 7.5$ Hz), 1.82 (m, 2H, $j = 7.3$ Hz), 1.64 (m, 2H, $j = 7.7$ Hz), 1.57 (m, 4H, $j = 7.5$ Hz), 1.47 (m, 2H, $j = 7.6$ Hz), 1.36 (m, 32H), 0.94 (t, 3H, $j = 7.3$ Hz), 0.88 (t, 3H, $j = 7.0$ Hz).

(b) ^1H NMR (600 MHz, CDCl_3): δ 7.08 (d, 2H, $j = 8.2$ Hz), 6.90 (d, 2H, $j = 8.8$ Hz), 6.80 (d, 2H, $j = 8.2$ Hz), 6.74 (d, 2H, $j = 8.9$ Hz), 3.91 (t, 2H, $j = 6.5$ Hz), 2.56 (t, 2H, $j = 7.7$ Hz), 2.50 (t, 4H, $j = 7.4$ Hz), 1.75 (m, 2H, $j = 7.3$ Hz), 1.57 (m, 2H, $j = 6.3$ Hz), 1.56 (m, 4H, $j = 6.0$ Hz), 1.45 (m, 2H, $j = 8.4$ Hz), 1.33 (m, 32H), 0.91 (t, 3H, $j = 7.4$ Hz), 0.88 (t, 3H, $j = 7.0$ Hz).

Fig. S1. (a) An NMR spectrum of the final product of the synthesis, assigned to *trans* Az. (b) An NMR spectrum of the product irradiated at 365 nm, assigned to *cis* Az.

1.2 UV-vis Absorption Spectra

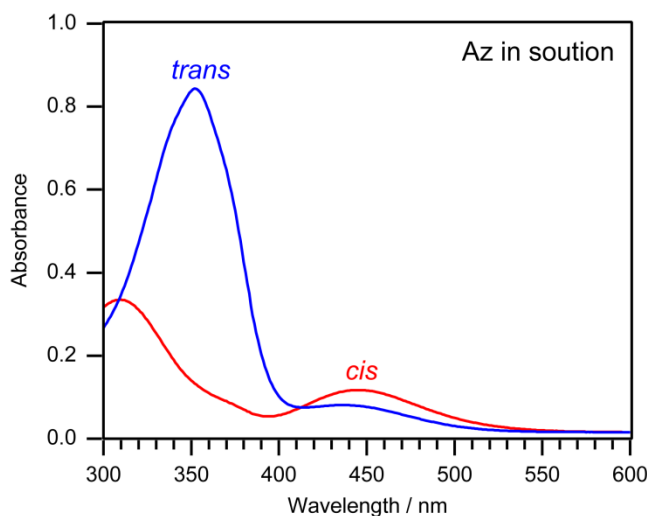


Fig. S2. UV-vis absorption spectra of *trans* Az and *cis* Az in dichloromethane (38 μM).

The final product was further characterised using UV-vis absorption spectroscopy. Fig. S2 shows the UV-vis absorption spectrum of the product (*trans* Az). Upon irradiation, the absorption band of *trans* Az at 352 nm ($S_2 \pi\pi^*$ state) markedly decreases and an absorption band of at 445 nm of *cis* Az ($S_1 n\pi^*$ state) appears. When the irradiation stopped, the absorption spectrum of *trans* Az was slowly restored due to thermal backisomerization.²

2. Density Functional Theory Calculations

As described in the manuscript, AuNPs move closer to each other upon isomerization of the Az tethered on the nanoparticles, resulting in more aggregation. The increased attraction between the AuNPs is driven by increased dipole-dipole interactions between Az when it converts from *trans* to *cis*. To test this idea, we performed density functional theory (DFT) calculations using the B3LYP functional with a basis set of LANL2DZ.³ Fig. S3 presents the optimized geometries of *trans* and *cis* Az along with their corresponding dipole moments. Since it is the azobenzene moiety that causes the change in the electric dipole moment of the molecule upon isomerization, we left out the alkyl sulfide part of the molecule in the calculation to lower the computation time. The left panel of Fig. S3 shows that the dipole moment of Az increases from 1.90 D to 4.87 D as the isomerization occurs from *trans* to *cis*, supporting our proposition. Our calculation results are consistent with previously reported values. For comparison, we list the dipole moments of various azobenzene derivatives calculated by other groups in Table S1.

Another significant observation is the redshifts of the N=N stretching modes in the SERS spectra of Az upon isomerization in the AuNP aggregates (Fig. 2 in the manuscript). We suggest that the N=N bond in the *cis* form of Az is more exposed and thus interacts with nearby AuNPs, weakening the bond. This model has been verified experimentally by the observation that the backisomerization of *cis* Az is much faster in AuNP aggregates than in solution (Fig. 4 in the manuscript). It is also supported by our harmonic frequency calculations. Fig. S3 shows that when the azobenzene moiety of Az binds to Au, the vibrational frequencies containing the N=N stretching character (denoted as $\nu(\text{NN})$ in red) shift to lower frequencies. Due to the use of Au atoms instead of AuNPs and the small size of the basis set, the calculated vibrational frequencies are far from perfect. Nonetheless, the calculation supports the pattern that the N=N stretching vibrational frequencies decrease when the N=N bond interacts with AuNPs.

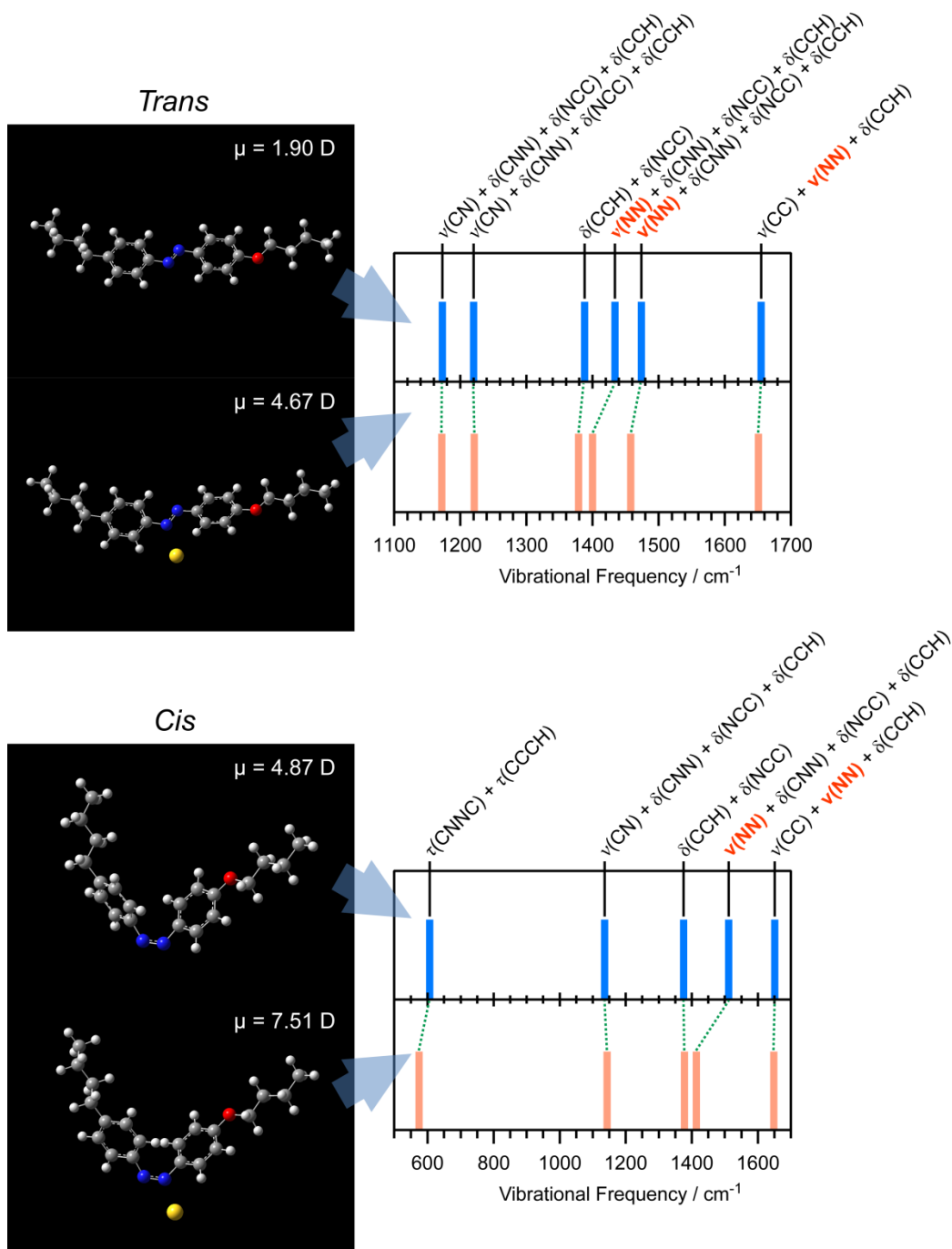
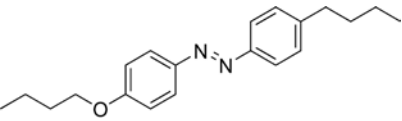
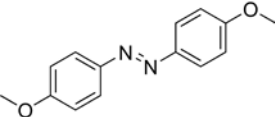
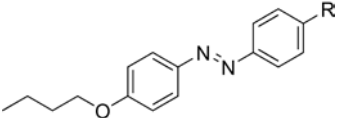
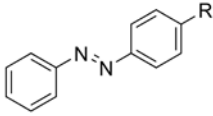
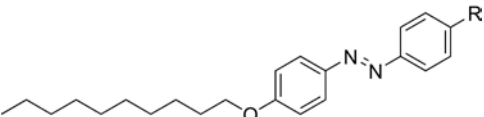


Fig. S3. Optimized geometries of *trans* Az (upper panel) and *cis* Az (lower panel), each free in vacuum and bound to Au through the N=N bond. The corresponding vibrational frequencies are presented on the right. The dipole moments (μ) of each structure are also included in the figure.

Table S1. Calculated dipole moments of *trans* and *cis* conformers of azobenzene derivatives.

Molecules	Calculation Method	Dipole Moments (D)		Reference
		<i>trans</i>	<i>cis</i>	
	B3LYP/LANLDZ	1.9	4.9	This work
	DNP/6-31G(d,p)	0	3.2	4
 R = Hexyl, CN	MM and AM1	1.21 (hexyl) 2.77 (CN)	4.92 (hexyl) 4.93 (CN)	5
 R = H, F, Br, CH ₃ , CF ₃ , <i>On</i> -Bu, <i>Ot</i> -Bu	B3LYP/6-31G**	0 (H) 1.52 (F) 1.89 (Br) 0.81 (CH ₃) 3.64 (CF ₃) 2.5 (<i>On</i> -Bu) 1.66 (<i>Ot</i> -Bu)	3.17 (H) 2.34 (F) 2.39 (Br) 3.63 (CH ₃) 2.66 (CF ₃) 4.39 (<i>On</i> -Bu) 3.26 (<i>Ot</i> -Bu)	6
 R = MeO, EtO, Hexyl, H, F, CF ₃ , CN	AM1	1.5 (H) 2.9 (F) 5.1 (CF ₃) 5.0 (CN)	4.4 (MeO) 4.6 (EtO) 4.5 (hexyl) 4.4 (H) 3.6 (F) 3.8 (CF ₃) 3.6 (CN)	7

3. Raman Spectral Evolution of *cis* Az in Solution and in AuNP Aggregates upon Thermal Backisomerization

Fig. 4 in the paper shows the change of the *cis* signature peak intensity for Az in the DCM solution and in the AuNP aggregates with time as photoinduced *cis* Az undergoes thermal backisomerization to *trans*. Here we present the spectral evolution for readers' reference. Fig. S4 presents selected Raman spectra of Az in the solution (left panel) and in the AuNP aggregates (right panel) acquired at the given time as *cis* Az isomerizes back to the *trans* form thermally in the dark. Fig. S4 clearly shows that the *cis* signature peak decays much faster for Az in the AuNP aggregates than free Az in the solution. Quantitative isomerization rates were obtained from the fitting of the decay with exponential functions as discussed in the paper (Fig. 4).

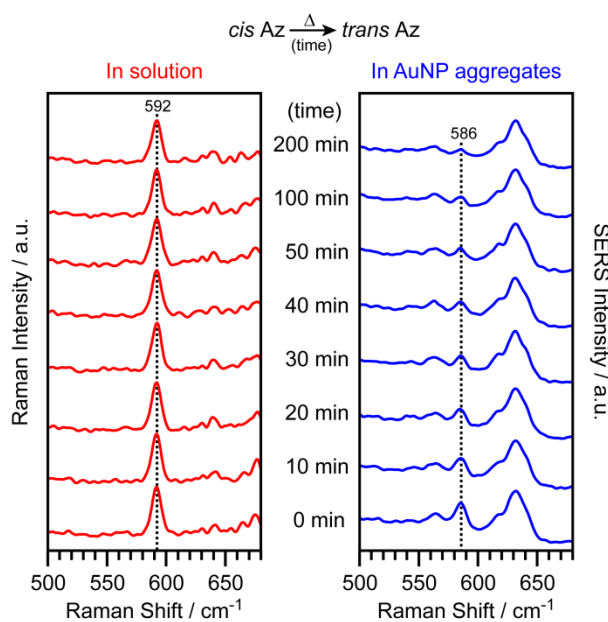


Fig. S4 Raman spectral evolution of Az in solution (left) and in AuNP aggregates (right) with elapsed time as *cis* Az undergoes thermal backisomerization to *trans* in the dark. The positions of the *cis* signature peaks (CNNC torsional mode) at 592 and 586 cm⁻¹ are denoted by dotted lines.

References

- (1) S. Peris, B. Tylkowski, J. C. Ronda, R. Garcia-Valls, J. A. Reina and M. Giamberini, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 5426.
- (2) J. H. Yoon and S. Yoon, *Bull. Korean Chem. Soc.*, 2009, **30**, 2877.
- (3) *Gaussian 03*, Wallingford, CT, 2004.
- (4) X. Tong, G. Wang, A. Soldera and Y. Zhao, *J. Phys. Chem. B*, 2005, **109**, 20281.
- (5) H. Akiyama, K. Tamada, J. Nagasawa, K. Abe and T. Tamaki, *J. Phys. Chem. B*, 2003, **107**, 130.
- (6) I. Vecchi, A. Arcioni, C. Bacchiocchi, G. Tiberio, P. Zanirato and C. Zannoni, *J. Phys. Chem. B*, 2007, **111**, 3355.
- (7) M. R. Han, Y. Hirayama and M. Hara, *Chem. Mater.*, 2006, **18**, 2784.