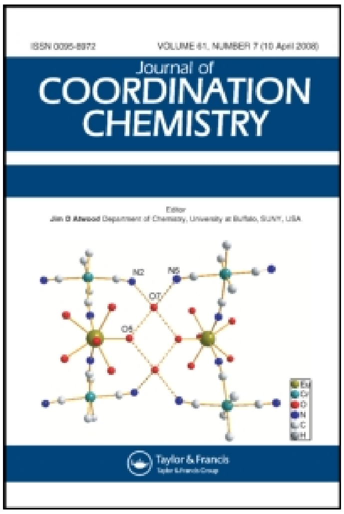

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Synthesis, crystal structure and photo-induced isomerization of [<i>N</i>,<i>N</i>'-<i>bis</i>(4-fluorobenzylidene) ethylenediamine]bromo(triphenylphosphine)copper(I) complex

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Synthesis, crystal structure and photo-induced isomerization of [*N*,*N*′-*bis*(4-fluorobenzylidene) ethylenediamine]bromo(triphenylphosphine)copper(I) complex

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The crystal structure of [N,N′-*bis*(4-fluorobenzylidene)ethylenediamine]bromo(triphenylphosphine)copper(I) ($C_{34}H_{29}BrCuF_2N_2P$) (**1**), a model compound for photoisomerization reactions which occur in photobiological processes such as vision, has been determined from X-ray diffraction data. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 19.1663(18)$, $b =$ [illegible].2456([illegible]3), $c =$ [illegible]1.9120([illegible]1) Å and $\alpha = 90°$, $\beta = 90.004(2)°$ and $\gamma = 90°$. The coordination polyhedron around copper(I) in this complex is best described as a distorted tetrahedron. Photochemical investigations in solution of the time resolved spectral changes, recorded before and after irradiation, show the transformation from *syn* to *anti* configuration of the C=N bond. Spectral profile and K rate constant were evaluated using multivariate curve resolution and non-linear least squares curve fitting by toolbox of MATLAB program using the corresponding absorption spectra-time data.

Keywords: Schiff base; Copper(I) complex; Tetrahedral; Photo-induced; Kinetic constant

1. Introduction

Schiff-base transition metal complexes have been studied extensively [1–8] and complexes with bidentate Schiff bases containing nitrogen and oxygen donor atoms play an important role in biological systems, representing models for metalloenzymes that catalyze the reduction of nitrogen and oxygen [9]. Schiff-base metal complexes have industrial, antifungal and biological applications [10]. The steric, electronic, and conformational effects imparted by coordinated ligands play an important role in modifying the properties of the prepared metal complexes. An understanding of these effects serves as the basis for rational design of complexes with specific and predictable properties. Although reports on [$Cu^I(N_4)$] complexes are numerous [11], limited work is related to the copper(I) complexes with mixed ligands, Cu(NN)XY [12, 13].

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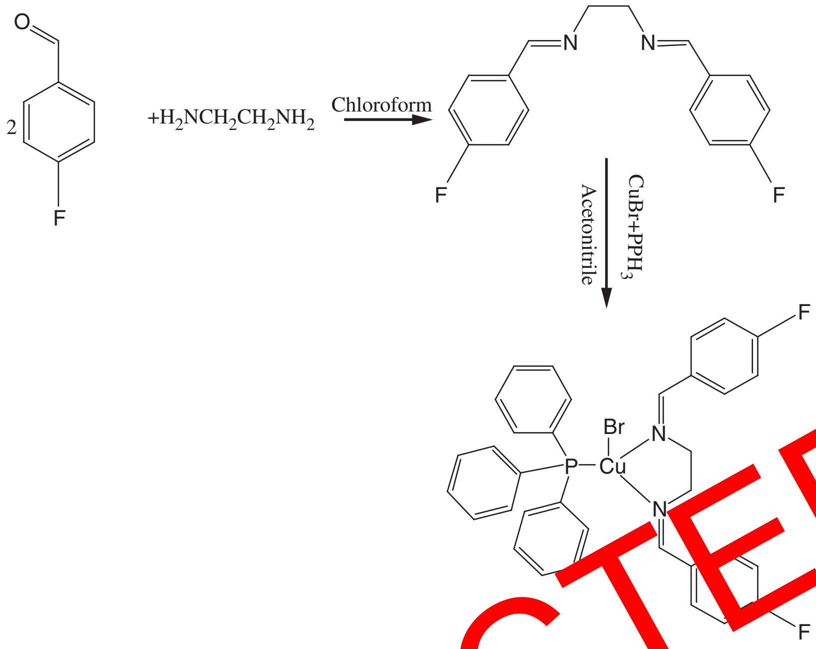


1

Scheme 1. Synthesis of [CuBr([illegible]en)(PPh$_3$)] (**1**).

Thermal [14–16] and photo [17–19] interconversions of *syn* and *anti* isomers of imines are a subject of long-standing interest. The mechanism for the thermal interconversion of imine diastereomers is the subject of considerable debate [20–22] regarding a planar inversion or rotation mechanism. The rotation or torsion mechanism involves twisting about the C=N double bond. In order to bring about this change in geometry, there must be a reduction in the double bond character of the imine bond in the transition state relative to the ground state. Multivariate curve resolution-alternating least squares (MCR-ALS) has already been applied to very diverse second-order calibration problems, for example, series of titrations, chromatographic runs or kinetic data [23–26]. In this research we report the synthesis, structural and photo-induced *syn*-*anti* isomerization of [*N*,*N*′-*bis*(4-fluorobenzylidene)ethylenediamine] bromo(triphenylphosphine) copper(I) (scheme 1).

2. Experimental

2.1. *Materials and physical measurements*

All chemicals were purchased from commercial sources and used as received without further purification. The infrared spectrum was obtained with a Shimadzu IR-435 spectrophotometer using a KBr pellet. The room-temperature visible absorption spectrum was recorded with a Shimadzu 160 spectrophotometer. NMR spectra were recorded on a Bruker AW 400 MHz. A high-pressure Hg lamp with grating

Table 1. Data collection and structure refinement parameters for **1**.

Chemical formula	$C_{34}H_{29}BrCuF_2N_2P$
Formula weight	678.04
Crystal color	Yellow
Temperature (K)	150(2)
λ (Å)	0.71073
Crystal system	Monoclinic
Crystal size (mm^3)	0.34 × 0.34 × 0.30
Space group	$P2_1/c$
Unit cell dimension (Å, °)	
a	19.1663(18)
b	13.2456(13)
c	11.9120(11)
α	90
β	90.004(2)
γ	90
V (Å^3)	3024.1(5)
Z	4
D_{Calcd} (g cm^{-3})	1.489
μ (mm^{-1})	2.135
$F(000)$	1376
Number of reflections collected	26681
Number of independent reflections (R_{int})	73[illegible] (0.0274)
Number of reflections used [$F^2 > 2\sigma$]	6178
Final R indices [$F^2 > 2\sigma$]	$R_1 = 0.$[illegible]252, $wR_2 =$ [illegible]583
Final R indices (all data)	$R_1 = 0.0$[illegible]3, $wR_2 = 0.0629$

monochromator was used in the photoisomerization. Singular value decomposition (SVD), multivariate curve resolution and non-linear least squares curve fitting were performed by MATLAB version [illegible].0.

2.2. *Synthesis of [CuBr(fb$_2$en)(PPh$_3$)] (1)*

At ambient temperature, a chloroform solution (5 mL) of ethylenediamine (14 mg, 0.23 mmol) was added to 4-fluorobenzaldehyde (57 mg, 0.46 mmol) in chloroform ([illegible] mL) with stirring. After half an hour, a mixture of CuBr (30 mg, 0.23 mmol) and PPh_3 (60 mg, 0.23 mmol) in acetonitrile (5 mL) was added to the above solution and stirred for an additional 20 min. Slow evaporation of the solvent under vacuum gave **1** as yellow crystals (scheme 1). The yield was 136 mg, 85%. IR (KBr pellet, 400–4000 cm^{-1}) 1620 (C=N). UV [chloroform; λ_{max} in nm (log ε in L mol^{-1} cm^{-1})]: 274 (6.44), 295 (6.47), 379 (6.59). ^{1}H NMR ($CDCl_3$) 3.86 (s, 4H, NCH_2CH_2N); 7.02–7.75 (m, 23H, ArH); 8.61 (s, 2H, 2CH=N).

2.3. *X-ray diffraction analysis*

Single crystal diffraction studies were carried out on a Bruker SMART 1K CCD diffractometer with Mo-Kα (0.71073 Å) radiation. The structure was solved by direct methods and the positional and anisotropic displacement parameters of the non-hydrogen atoms were refined by least-squares calculation on F^2. A summary of the crystal data along with further details of the structure determination and refinement are given in table 1. The unit cell parameters were determined using SMART [27] and refined based on the positions of all strong reflections using SAINT [27].

Absorption correction was by SADABS [28] based on symmetry-equivalent and repeated reflections. The structure was solved by direct methods using SIR97 [29] and refined by full matrix least-squares on F^2 using SHELXTL [30]. Molecular graphics were produced using DIAMOND-3 [31] and Mercury 1.4 [32].

3. Results and discussion

3.1. *Crystal structure of [CuBr(fb$_2$en)(PPh$_3$)] (1)*

Compound **1** crystallizes in the monoclinic crystal system with space group $P2_1/c$. The solid-state structure consists of a distorted tetrahedral geometry around copper with an N_2PBr donor set (figure 1). Selected bond lengths and angles are given in table 2.

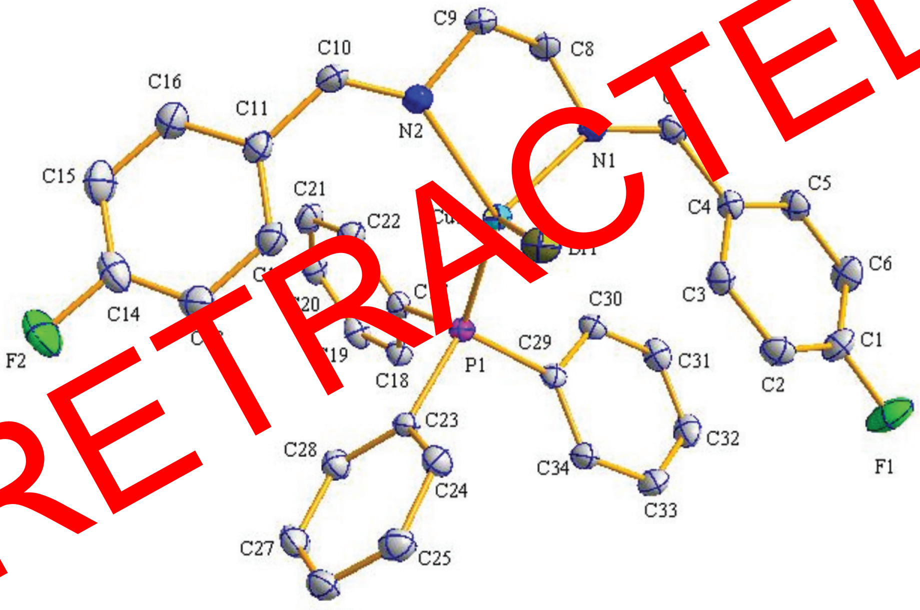


Figure 1. ORTEP structure of **1**, showing the thermal ellipsoids at 50% probability. All H atoms have been omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°).

Cu–N1	2.1322(14)	N1–C7	1.277(2)
Cu–N2	2.0912(15)	N1–C8	1.476(2)
Cu–P	2.2048(5)	N2–C9	1.470(2)
Cu–Br	2.4789(3)	N2–C10	1.276(2)
C8–C9	1.516(3)	F(1)–C(1)	1.362(2)
N1–Cu–N2	84.07(6)	N2–Cu–P	125.10(4)
N1–Cu–Br	107.24(4)	Br–Cu–P	117.682(15)
N2–Cu–Br	99.22(4)	C8–N1–C7	115.76(15)
N1–Cu–P	117.69(4)	C8–N1–Cu	105.67(11)

Tetrahedral geometry is expected for four-coordinate copper(I), but the coordination sphere around copper(I) in **1** is distorted by the restricting bite angle of the chelating ligand. The N(1)–Cu–N(2) angle in **1** is 84.07(6)° and the Br–Cu–P angle is 117.682(15)°. The dihedral angles between the various benzene rings within the molecule are: C11–C16/C1–C6 = 44.73°, C11–C16/C23–C28 = 45.50°, C29–C34/C23–C28 = 75.25° and C29–C34/C17–C22 = 70.97°. The crystal packing in **1**, viewed along the *b* axis, showing four molecules is given in figure 2. The benzene rings of **1** are stacked *via* π–π interactions, having a centroid-to-centroid distance of 3.595 Å and C9–H9A $\cdots$ π distance of 2.566 Å, as shown in figure 3. In the crystal packing, the molecules are linked via weak intermolecular C–H $\cdots$ F and C–H $\cdots$ Br hydrogen bonds (figure 4). Intermolecular hydrogen bonds occur between H(16A) and F(1) (2.51(1) Å) and between H(9B) and Br(1) (3.41(1) Å), H(10A) and Br(1) (2.94(1) Å) (table 3). The Cu–Br bond length of 2.4789(3) Å in **1** is slightly longer than those reported (for example: 2.4400(5) and 2.3312(3) Å for [CuBr(ca$_2$en)(PPh$_3$)] and [CuBr(bipyridine)(PPh$_3$)], respectively [13, 14]. The Cu–P distance of 2.2048(5) Å agrees well with the corresponding data in related complexes [12].

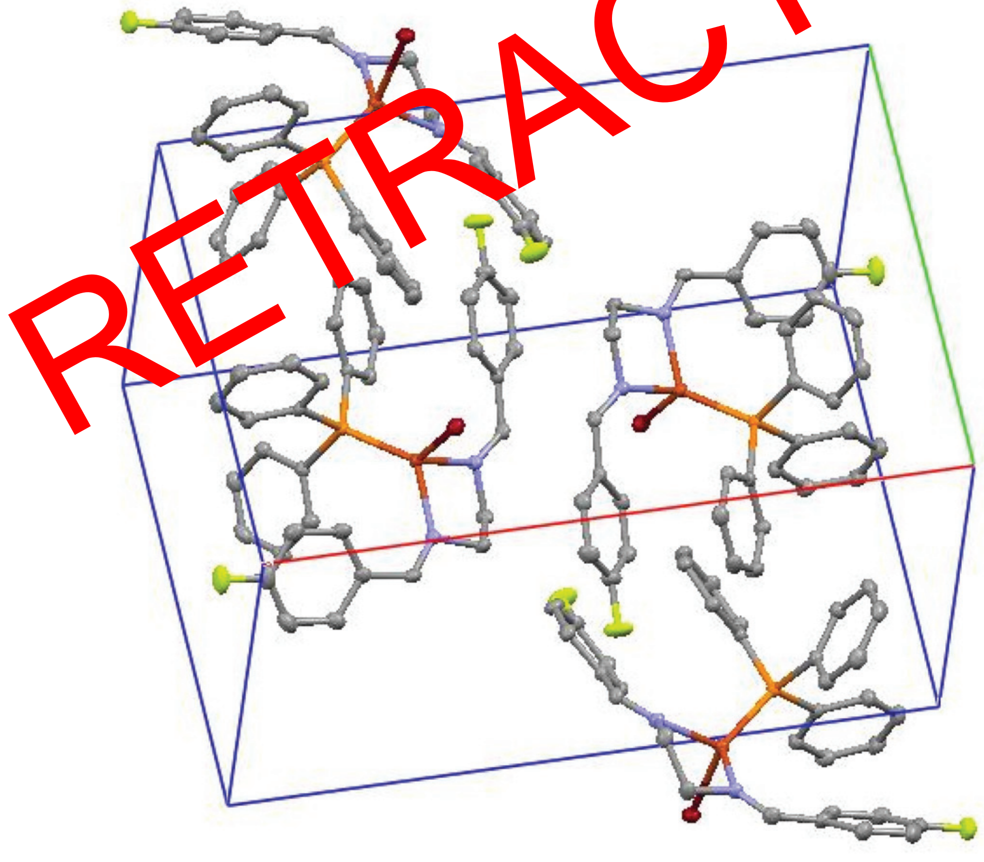


Figure 2. The crystal packing in **1**, viewed along the *b* axis, showing four molecules.

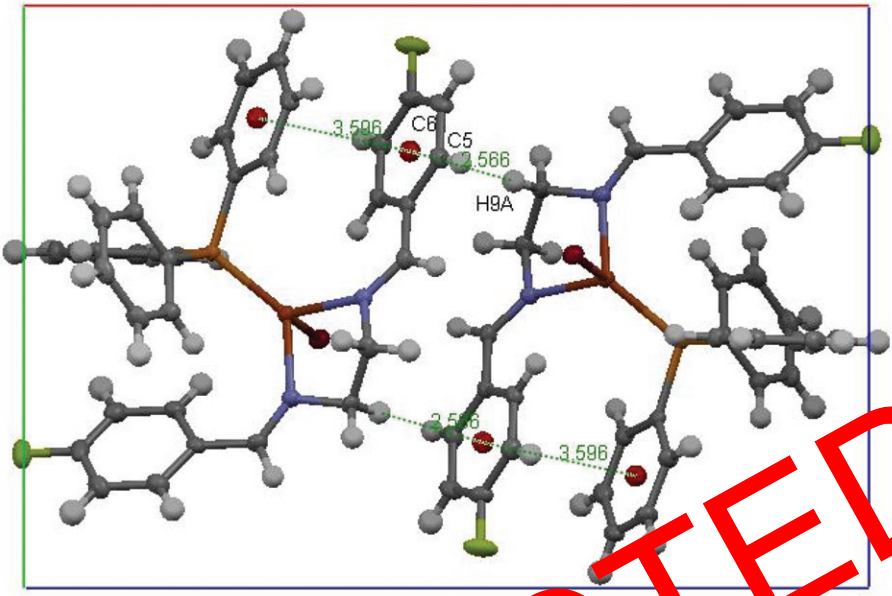


Figure 3. The stacking of molecule of **1** via π–π, C–H···π interactions.

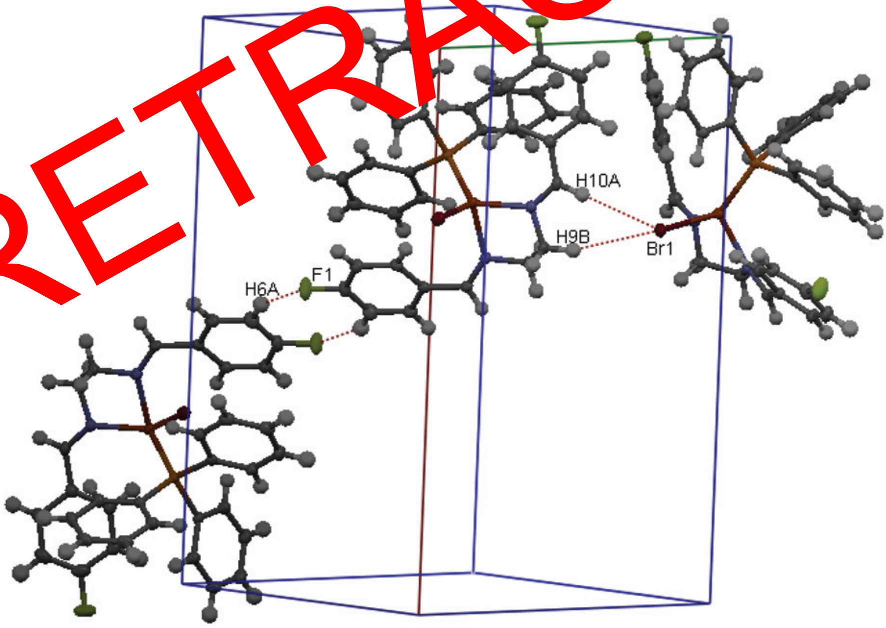


Figure 4. The C–H···F and C–H···Br hydrogen bonds of **1**.

3.2. *Photoisomerization of 1*

The spectrum of the free ligand showed major peaks at 251 and 301 nm, identified as characteristic $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ absorption bands; the spectrum of **1** showed two

Table 3. Hydrogen-bonding geometry (Å, °).

D–H···A	D–H	H···A	D···A	D–H···A
C16–H16A···F1^{i}	0.95(1)	2.51(1)	3.390(19)	154.69(1)
C9–H9B···Br1^{ii}	0.99(1)	3.41(1)	4.002(19)	162.49(1)
C10–H10A···Br1^{ii}	0.95(1)	2.94(1)	3.827(19)	156.82(1)

Symmetry codes: (i) $1-x$, $-y$, $1-z$; (ii) x, $1.5-y$, $1/2+z$.

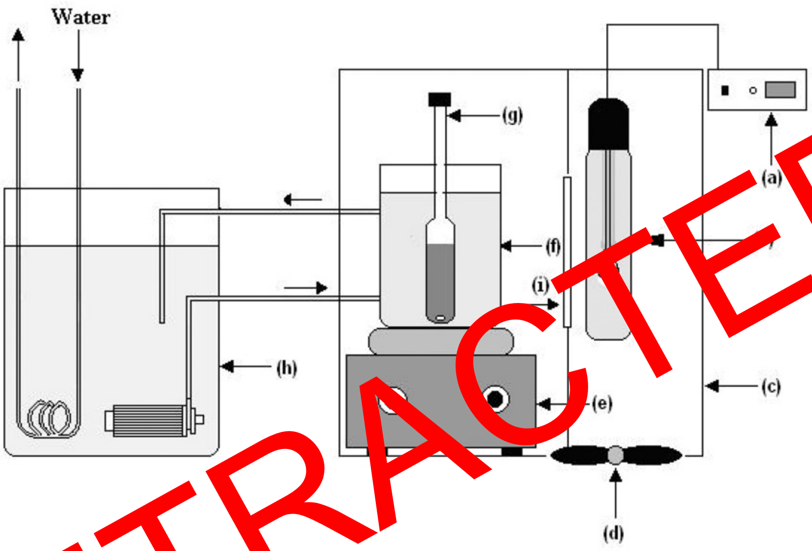


Figure 5. Photolytic setup; (a) power supply; (b) high-pressure Hg lamp; (c) photoreactor with aluminum foil as reflector for a full irradiation of catalyst; (d) fan; (e) magnetic stirrer; (f) 2L Pyrex beaker; (g) photolytic cell; (h) water thermostat (Haake model F 122); (i) monochromator.

Major peaks, one at 295 nm related to a ligand centered transition of the coordinated syn isomer of *N*,*N*′-*bis*(4-fluorobenzylidene)ethylenediamine in solution, and another at 379 nm which is identified as MLCT. Irradiatiing the chloroform solution of **1** with a high pressure mercury lamp (figure 5), the absorption maximum of **1** at 295 nm decreased and 379 nm increased with an isobestic point at 355 nm (figure 6). The shift indicates the transformation from *syn* to *anti* configuration of the C=N bond of the coordinated ligand in solution (scheme 2).

3.3. *Kinetic constants and quantum yields*

As any other resolution method, the aim of MCR-ALS is the optimal decomposition of a data matrix $\boldsymbol{D}$ into the product of two small matrices, $\boldsymbol{C}$ and $\boldsymbol{S}^{\mathrm{T}}$. This decomposition is the result of the validity of Beer-Lambert's law for absorption measurements. $\boldsymbol{D}=\boldsymbol{C}\boldsymbol{S}^{\mathrm{T}}+\boldsymbol{E}$, $\boldsymbol{D}$ is the original measurement and contains as rows the absorption spectra measured as a function of reaction time. The matrices $\boldsymbol{C}$ and $\boldsymbol{S}^{\mathrm{T}}$ contain, as columns, the kinetic profiles of the compounds involved in the process and, as rows,

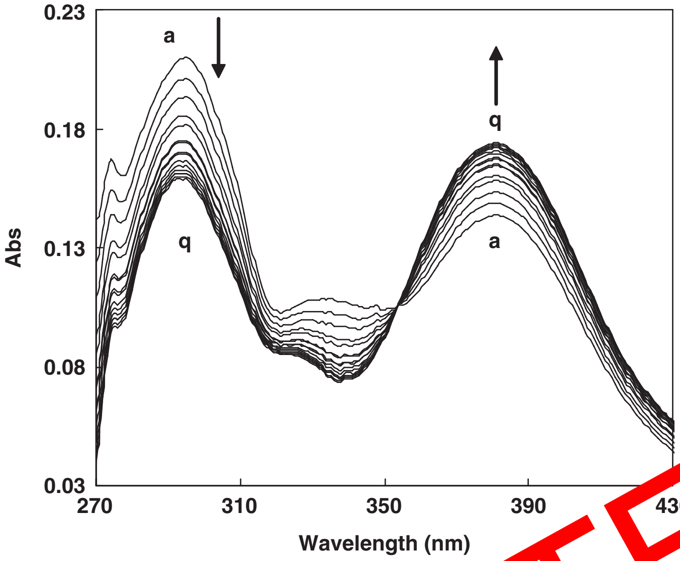
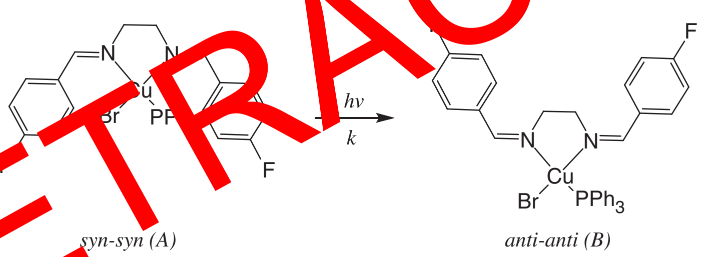


Figure 6. UV–Vis absorption spectral changes for 0.10 mM **1** with UV irradiation in chloroform. From a to q, each irradiation time = 2 min; total, 40 min.



Scheme 2. Photoisomerization mechanism of **1** in chloroform.

their related spectra, respectively. ***E*** is the error-related matrix. Decomposition of the ***D*** matrix is achieved by iterative optimization under suitable constraints for ***C*** and $\boldsymbol{S}^T$. Spectra profiles were evaluated using MCR-ALS. The best MCR-ALS results were obtained by assuming two components for **1** defined by applying the constraints of non-negativity (for both concentrations and signals), unimodality of the concentrations, and closure (the sum of the concentrations of the isomers). Under such conditions, a lack of fit of 0.33% was obtained for **1**. The calculated concentration profiles are shown in figure 7 for **1**. Kinetic constants were evaluated using non-linear least squares curve fitting by toolbox of MATLAB using the concentration profiles and definition of exponential function (fitted exponential curve shown in figure 7 by the solid lines). For **1**, the obtained kinetics constant value is $1.1 \times 10^{-1}\,\mathrm{min}^{-1}$ (RMSE = 6.9×10^{-4}) (RMSE is root mean squares of errors).

Quantum yield is a useful parameter to indicate the efficiency of a photochemical reaction, which is defined as the number of probe molecules undergoing a specific chemical reaction divided by the number of photons absorbed. The quantum yield of photoisomerization can be calculated from the observed first-order rate constant,

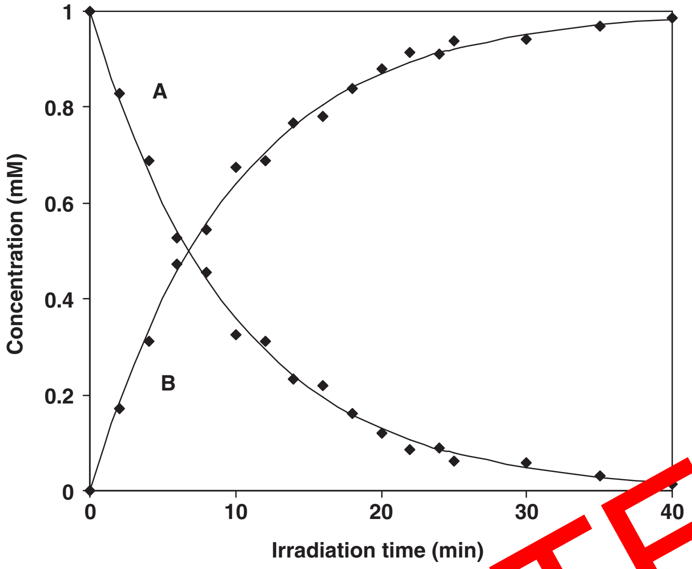


Figure 7. The concentration profiles of *syn-syn* (A) and *anti-anti* (B) isomers of **1** in chloroform [MCR-ALS (◆) and fitted exponential function (solid lines)].

where a specific form of quantum yield, ϕ based on first-order kinetics was indicated in equation (1) [35]:

$$\phi = \frac{k}{2.303 I_{0,\lambda} \varepsilon_\lambda l} \qquad (1)$$

with $I_{0,\lambda}$ the incident light intensity at specific wavelength (Einstein $l^{-1}\,s^{-1}$). According to the data provided by the Southern New England Ultraviolet Company, intensity of 350 nm is 3.1 × 10^{-6} (24 W) E $l^{-1}\,s^{-1}$, ε_λ = molar absorptivity of compounds at 350 nm and l = cell path length (1 cm). The quantum yield value obtained for **1** is 0.246.

Supplementary material

Crystallographic data, tables of atomic coordinates and thermal parameters, and full lists of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 658010 for **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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