

# The Control of Photochromism of [3H]-Naphthopyran Derivatives with Intramolecular CH– $\pi$ Bonds

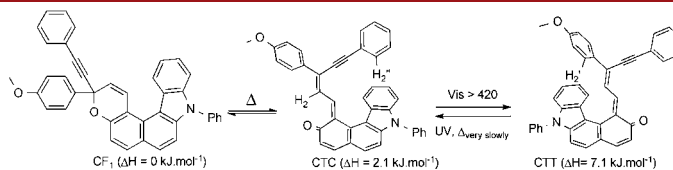
Michel Frigoli,<sup>\*,†</sup> Francois Maurel,<sup>‡</sup> Jérôme Berthet,<sup>§</sup> Stéphanie Delbaere,<sup>§</sup> Jérôme Marrot,<sup>†</sup> and Maria. M. Oliveira<sup>||</sup>

ILV, CNRS UMR 8180, Université de Versailles, Versailles, France, ITODYS, CNRS UMR 7086, Université Paris, Paris, France, UDSL, CNRS UMR 8516, University Lille Nord de France, Lille, France, and CQ-VR, Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal

michel.frigoli@chimie.uvsq.fr

Received July 2, 2012

## ABSTRACT



The photochromism of [3H]-naphthopyran derivatives can be switched from T-type to inverse- or P-type through the manipulation of relative thermodynamic stabilities of open isomers with intramolecular CH– $\pi$  bonds.

Photoswitchable molecules such as azo compounds and dithienylethenes have been extensively investigated in recent years, due to their potential in technological advanced applications ranging from molecular electronics to bio-imaging.<sup>1</sup> These applications rely on the capacity of the photochromic compounds to switch reversibly between two states thermally (meta)stable having different properties by light (P-type photochromism).<sup>2</sup> In contrast, photochromic organic naphthopyrans have attracted much attention due to their industrial application in ophthalmic technology.<sup>3</sup> The reversible change of color under solar exposition that ceases after the removal of the illumination constitutes the first required property for the use of

naphthopyrans in plastic photochromic lenses (T-type photochromism). Changing the photochromism of naphthopyrans from T- to P-type is very challenging and would offer a new family of photochromes that could be of critical use in advanced applications and constitute an interesting alternative to azocompounds and dithienylethenes. The photochromism of [3H]-naphthopyrans is believed to start with C–O bond cleavage of the closed pyran ring (CF) induced by UV absorption that leads after some internal rearrangement of double bond to an open colored isomer transoid-cis (TC) which returns thermally to the initial state (Scheme 1).<sup>4</sup> Under continuous irradiation, TC can eventually produce a transoid-trans open isomer (TT) following isomerization of one double bond.<sup>4</sup> The reversible change of color comes from the fact that the TC isomer is the major product under solar or UV irradiation.<sup>5</sup> In fact, TC and TT isomers differ from their thermal and thermodynamic stabilities. In the case of the reference compound namely the 3,3-diphenyl-[3H]-naphtho[2,1-*b*]pyran at rt in toluene solution, TC is less thermally stable by ~3–4 orders of magnitude compared to TT while its thermodynamic stability is ~8.9 kJ higher than that of TT.<sup>6</sup>

<sup>†</sup> Université de Versailles.

<sup>‡</sup> Université Paris.

<sup>§</sup> University Lille Nord de France.

<sup>||</sup> Universidade de Trás-os-Montes e Alto Douro.

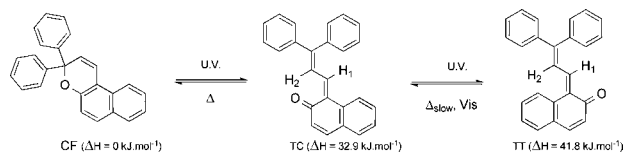
(1) Selected reviews and books on photochromism and applications: (a) Irie, M. *Chem. Rev.* **2000**, *100*, 1685. (b) *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, 2001. (c) Tian, H.; Feng, Y. *J. Mater. Chem.* **2008**, *18*, 1617. (f) Tian, Z.; Wu, W. A.; Li, D. Q. *ChemPhysChem* **2009**, *10*, 2577. (d) Russev, M.-M.; Hecht, S. *Adv. Mater.* **2010**, *22*, 3348. (e) Beharry, A. A.; Woolley, G. A. *Chem. Soc. Rev.* **2011**, *40*, 4422.

(2) Bouas-Laurent, H.; Dürr, H. *Pure Appl. Chem.* **2001**, *73*, 639.

(3) Reviews on photochromic naphthopyrans: (a) Van Gemert, B. In *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Guglielmetti, R. J., Eds.; Kluwer Academic/Plenum Publishers: New York, 1999; Vol. 1, Chapter 3. (b) Hepworth, J. D. Heron, B. M. *Functional Dyes*; Sung-Hoon, K., Ed.; Elsevier: Amsterdam, 2006. (c) Corns, N. S.; Partington, S. M.; Towns, A. D. *Color. Technol.* **2009**, *125*, 249.

(4) (a) Delbaere, S.; Luccioni-Houze, B.; Bochu, C.; Teral, Y.; Campredon, M.; Vermeersch, G. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1153. (b) Ottavi, G.; Favaro, G.; Malatesta, C. *J. Photochem. Photobiol., A* **1998**, *115*, 123.

**Scheme 1.** Photochromic Interconversion in [3H]-Naphthopyran



Indeed, a H-bond is established between proton H2 and the oxygen of the ketone group stabilizing TC while the same proton in TT is in a repulsive interaction with the naphthalene ring, consequently destabilizing TT. The isomerization of the double bond involved in the formation of TT from TC is rendered more difficult due to the presence of this H-bond that should be broken in this transformation. Thus, the photochromism of naphthopyran is controlled by a H-bond allowing the accumulation of the most thermodynamic stable open isomer TC. According to this argument, the manipulation of the relative thermodynamic stabilities of open isomers compared to the closed form would in principle modify the thermo-/photoequilibrium between all species involved in the photochromic processes.

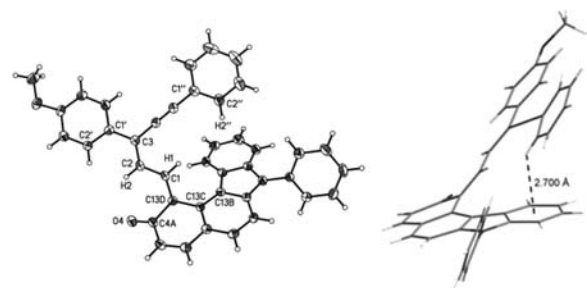
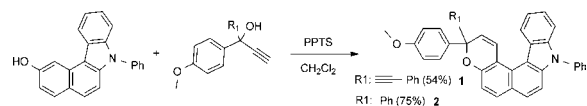
Herein, we report the synthesis and the properties of two naphthopyran derivatives **1** and **2** displaying unusual and intriguing inverse- and P-type photochromism respectively, through the adjustment of relative thermodynamic stabilities of open isomers with CH– $\pi$  bonds. To the best of our knowledge, the control of the photochromism of naphthopyrans with CH– $\pi$  bonds is the first time demonstrated and sheds further insight into the molecular design of naphthopyrans with specific and innovative properties. Compounds **1** and **2** namely belong to benzopyrano[6,5-*c*]carbazole derivatives which differ from one substituent located at the 3-position. **1** has an ethynylphenyl group while this group is replaced by a phenyl substituent in **2**. This little structural change has a tremendous effect on the thermo-/photoequilibrium between the closed and open isomers.

The preparation of **1** and **2** is outlined in Scheme 2. The building of the naphthopyran scaffold in **1** and **2** was

(5) Selected references: (a) Guo, K. P.; Chen, Y. *J. Mater. Chem.* **2010**, *20*, 4193. (b) Frigoli, M.; Pimienta, V.; Moustrou, C.; Samat, A.; Guglielmetti, R.; Aubard, J.; Maurel, F.; Micheau, J. C. *Photochem. Photobiol. Sci.* **2003**, *8*, 888. (c) Venec, D.; Delbaere, S.; Micheau, J. C.; Frigoli, M.; Moustrou, C.; Samat, A.; Vermeersch, G. *Photochem. Photobiol., A* **2006**, *181*, 174. (d) Tulyakova, E. V.; Fedorova, O. A.; Micheau, J. C.; Paramonov, V.; Lokshin, V.; Vermeersch, G.; Delbaere, S. *ChemPhysChem* **2011**, *12*, 1294. (e) Gabbutt, C. D.; Heron, B. M.; Instone, A. C. *Tetrahedron* **2006**, *62*, 737. (f) Ortica, F.; Smimmo, P.; Favaro, G.; Mazzucato, U.; Delbaere, S.; Venec, D.; Vermeersch, G.; Frigoli, M.; Moustrou, C.; Samat, A. *Photochem. Photobiol. Sci.* **2004**, *3*, 878. (g) Frigoli, M.; Mehl, G. H. *Chem. Commun.* **2004**, 2040. (h) Oliveira, M. M.; Salvador, M. A.; Delbaere, S.; Berthet, J.; Vermeersch, G.; Micheau, J. C.; Coelho, P. J.; Carvalho, L. M. *J. Photochem. Photobiol., A* **2008**, *198*, 242. (i) Coelho, P. J.; Salvador, M. A.; Oliveira, M. M.; Carvalho, L. M. *J. Photochem. Photobiol., A* **2005**, *172*, 300. (j) Sallenave, X.; Delbaere, S.; Vermeersch, G.; Saleh, A.; Pozzo, J.-L. *Tetrahedron Lett.* **2005**, *46*, 3257.

(6) (a) Demadrille, R.; Rabourdin, A.; Campredon, M.; Giusti, G. *J. Photochem. Photobiol., A* **2006**, *168*, 143. (b) Gabbutt, C. D.; Heron, B. M.; Instone, A. C.; Kolla, S. B.; Mahajan, K.; Coelho, P. J.; Carvalho, L. M. *Dyes Pigm.* **2008**, *76*, 24. Relative energies of all isomers for the reference was calculated by DFT calculation (SI).

**Scheme 2.** Synthesis of Photochromic Compounds **1** and **2**



**Figure 1.** X-ray molecular structure of CTC isomer.

obtained by a “one-pot reaction” with 7-phenyl-7H-benzo[*c*]carbazol-2-ol and the corresponding prop-2-yn-1-ol derivatives in the presence of a catalytic amount of PPTS.<sup>7</sup> For **2**, the reaction proceeded smoothly and the closed form **CF2** was obtained as a pure product in 75% yield. In the case of **1**, the reaction mixture became redder, and after 24 h of stirring, analysis with a TLC plate revealed a dark red spot as the main product. This was very surprising and indicative that colored open isomers were stable in the reaction mixture. **1** could be purified by column chromatography with a mixture of petroleum ether and ethylacetate (90/10) as eluent and obtained as a dark red solid in 54% yield. <sup>1</sup>H NMR spectrum at 20 °C in toluene solution amazingly revealed the presence of only two isomers (80/20 ratio). Four open isomers could be expected for naphthopyrans having a chiral center at the 3-position. The minor isomer was assigned to **CF1** due to the doublet signal at 6.00 ppm (*J* = 9.1 Hz), characteristic of proton H2 of the pyran ring (Figure 2S and Table 1S, Supporting Information (SI)). For the major isomer, two pseudodoublets at 9.26 and 9.39 ppm with a coupling constant of 12.2 Hz in the AB system were observed. The measured values of the coupling constant and downfield chemical shifts make it possible to attribute these signals to protons H2 (deshielded by C=O) and H1 (deshielded by the concomitant effect of the ethynyl and indolino group) in TC-type compound isomers.<sup>4a,5c–5f</sup> The major isomer was found to be a CTC isomer, and this assignment was based on a 2D-NOESY experiment (Figure 6S, SI).

The structure of the CTC isomer was nicely confirmed by X-ray crystallography (Figure 1).<sup>8</sup> We were very pleased

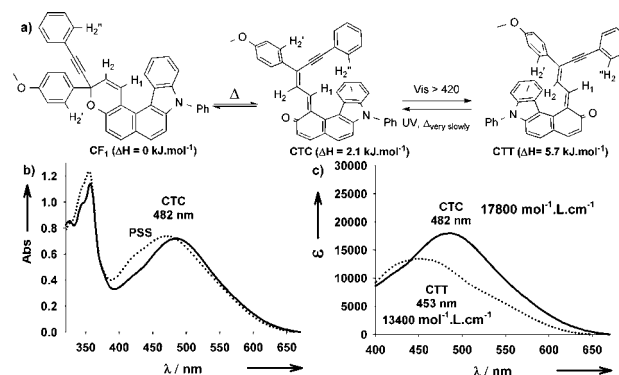
(7) Frigoli, M.; Moustrou, C.; Samat, A.; Guglielmetti, R. *Eur. J. Org. Chem.* **2003**, 2799.

(8) X-ray data file is available in Cambridge database under deposition number CCDC 885269.

to get the first X-ray molecular structure of one open isomer in the naphthopyran series. It is worth noting that the distance between H2 and the ketone group is  $\sim 2.31$  Å, the angle C2–H2–O is  $122.25^\circ$ , and the dihedral angle between C4a–O–H2–C2 is  $21.37^\circ$ , confirming a strong H-bond is taking place in the TC isomer.<sup>9</sup> The alternate bond lengths of the diene unit between the double (C3–C2 = 1.36 Å), pseudosingle (C2–C1 = 1.43 Å), and double bond (C1–C13d = 1.36 Å) are in agreement with a conjugated bridge and a quinoidal structure of the open form.<sup>8</sup> This is also consistent with the bond length of the conjugated ketone group (1.22 Å).<sup>9</sup> Due to the repulsive interaction between H1 and the indoline group, a dihedral angle (C13b–C13c–C13d–C1) of  $32^\circ$  between the diene and the pseudonaphthalene units is observed. Thanks to the ethynyl group, the anisole is almost perfectly planar with the conjugated bridge (C2–C3–C1'–C2' =  $4.65^\circ$ ) and the phenyl group is slightly more twisted from planarity (C2–C3–C1''–C2'' =  $7.53^\circ$ ). Indeed, the twisting of the phenyl group comes from the dedication of this group to be in a strong edge-to-face interaction with the phenyl of the carbazole unit. The geometry of the edge-to-face interaction is as follows: the proton H2'' in interaction to ring centroid distance is 2.70 Å, and the dihedral angle between the interacting ring planes is  $51.77^\circ$ . These bond lengths and angles are typical for strong edge-to-face interactions with face-tilted-T geometry.<sup>10</sup>

According to the X-ray structure, the introduction of the ethynyl group at the 3-position leads to a very good conjugation throughout the entire molecule by limiting the steric hindrance at the strict minimum. The concomitant effect of a planar structure highly conjugated and the withdrawing character of the ethynyl group<sup>11</sup> with the presence of a strong CH– $\pi$  bond led to the first thermo-equilibrium between CF1 and CTC wherein the CTC is the most abundant isomer (Figure 2a).

The photochemical interconversion of **1** was carried out in toluene solution at 20 °C and followed by UV/vis and NMR spectroscopies. Before irradiation, the system **1** displays a strong red color centered at 482 nm, ascertained to the absorption behavior of CTC. Knowing the concentration of CTC, an  $\epsilon$  value of  $17800 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$  at 482 nm was deduced. Upon irradiation with UV light, the absorption did not change at all. In contrast, upon visible irradiation, a blue shift of the maximum band was observed (Figure 2b). The change of absorbance was indicative that CTC photoisomerized into a less conjugated open isomer. NMR spectrum at the PSS state obtained after 5 min of irradiation, indicates the exclusive formation of CTT isomer (Figure 2, Figure 5S, SI). The difference in the NMR spectra of CTC and CTT confirmed the presence of the CH– $\pi$  bond between proton H2'' and the phenyl of the carbazole unit in CTC as seen in the X-ray molecular structure. The chemical shift of proton H2'' (6.78 ppm) in CTC is upfield compared to H2'' in CTT (7.70 ppm). This



**Figure 2.** (a) Thermo- and photoequilibrium for **1**. (b) Absorption spectra before and after visible irradiation. (c) Absorption spectra of CTC and CTT in the visible range.

strong upfield effect is the NMR signature of a strong CH– $\pi$  bond between H2'' and the phenyl of the carbazole in CTC.<sup>10</sup> A similar upfield effect was observed between the chemical shifts of proton H2' (7.11 ppm) in CTT and H2' (8.01 ppm) in CTC. This demonstrates that a strong edge to face interaction between the anisole and the phenyl of the carbazole is taking place in the CTT isomer as well. In our experimental conditions, at PSS state, the photo-equilibrium was comprised of CF1 (10%), CTC (37%), and CTT (53%). Knowing the percentage of all isomers before and after irradiation, it was possible to calculate the absorption property of CTT in the visible region. The absorption maximum of CTT is 453 nm with an  $\epsilon$  value of  $13400 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ . Compared to CTC, the absorption maximum is blue-shifted with a lower  $\epsilon$  value. This is indicative of a lower conjugation which might result from the fact that the steric repulsion between H-2 and the carbazole is more important in CTT than that between H-1 and the carbazole in CTC. Optimized geometries at the CAM-B3LYP/6-311G(d,p) level of CTT and CTC indicate that the dihedral angle between the diene unit and the pseudonaphthalene core (C13b–C13c–C13d–C1) for CTT is  $40.8^\circ$  and  $34.4^\circ$  for CTC, respectively (Table 2S, SI). Therefore, the overlapping of the  $\pi$ -electrons should be less efficient in TT than in TC isomers and might be responsible for the absorption difference observed between CTC and CTT.

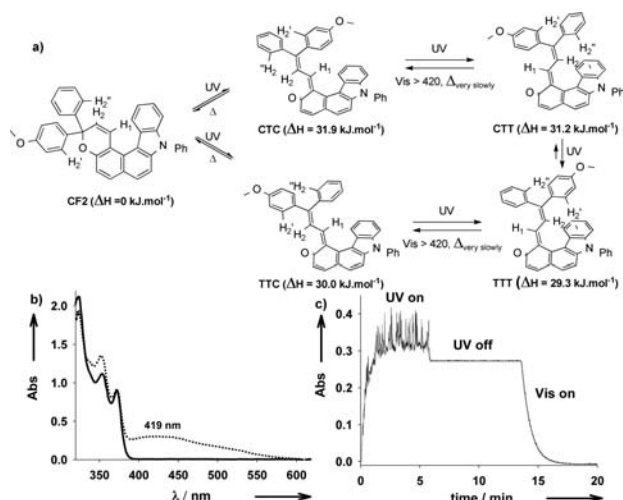
Under UV irradiation, CTT could be converted back to CTC. After 20 min of irradiation, the photoequilibrium was comprised of CF1 (10%), CTC (75%), and CTT (15%) (Figure 8S, SI). Moreover, the thermal stability of CTT is amazingly high as, after 1 month at rt, only 24% of CTT disappeared to give CTC (Figure 9S, SI). In order to gain insight into the effect of the ethynyl group and CH– $\pi$  bonds, we carried out DFT calculations to determine the relative energy between all isomers (Figure 2). The order of stability given in  $\text{kJ} \cdot \text{mol}^{-1}$  was as follows: CF1 > CTC ( $\Delta H = 2.1$ ) > CTT ( $\Delta H = 5.7$ ) > TTC ( $\Delta H = 18.9$ ) > TTT ( $\Delta H = 20.3$ ). The order of stability is correlated in some way to the efficiency of the conjugation throughout the whole molecule which is well represented by the

(9) Desiraju, G. *Chem. Res.* **1991**, *24*, 290.

(10) Jennings, W. B.; Farrell, B. M.; Malone, J. F. *Acc. Chem. Res.* **2001**, *34*, 885.

(11) Lucas, X.; Quiñero, D.; Frontera, A.; Deyà, P. M. *J. Phys. Chem. A* **2009**, *113*, 10367.





**Figure 3.** (a) Photochemical interconversion for **2**. (b) Absorption spectra before and after UV irradiation. (c) Absorption changes at 419 nm upon UV then upon visible light.

dihedral angle between the anisole and the diene unit (C2–C3–C1'–C2') (Table 3S, SI). Also, CTC and CTT are stabilized by a CH– $\pi$  bond. This explains why CF1 and CTC are in thermal equilibrium. The small difference in energy between these two forms indicates a barrierless thermoisomerization between CF1 and CTC.<sup>12</sup> System **1** is the first example of inverse-type photochromism in the naphthopyran series in which visible irradiation induces isomerization from CTC to CTT that leads to a blue shift of the absorption and the original absorbance is retrieved by UV irradiation. This original behavior has been possible due to the electronic and steric effect of the ethynyl group at the 3-position and the important presence of the CH– $\pi$  bond occurring in open isomers.

For **2**, before irradiation, the closed form absorbs exclusively in the UV region and the solution is colorless. Upon continuous UV irradiation, the solution turns from colorless to yellow. The maximum of the visible band was 419 nm (Figure 3b). After reaching the PSS state, the irradiation was removed and the change of absorbance was monitored at 419 nm at rt in the dark (Figure 3c). A fast bleaching rate constant ( $k = 0.21 \text{ s}^{-1}$ ) was first observed, accounting for 7% of total absorbance, attributed to TC isomers. 93% of the residual absorbance was found to very stable for a long period of time ( $k = 1.01 \times 10^{-6} \text{ s}^{-1}$ ,  $t_{1/2} = 380 \text{ h}$ ). The stable coloration was attributed to the absorption of TT isomers. The reaction back from TT to CF2 can be induced photochemically with visible light. This photochemical process involves two consecutive transformations, TT→TC→CF, the first one being the rate limiting step.<sup>5h,i</sup> **2** can be considered as a P-type photochromic system in which coloration and bleaching

can be obtained photochemically. Even though TT isomers revert back to the closed form thermally, this thermal process is rather slow with the half-life comparable to those of azocompounds.<sup>1f</sup> To confirm the photoproducts produced under UV irradiation, NMR spectra before and after irradiation at rt were recorded. After UV irradiation, two open isomers were observed and were attributed to TTT and CTT isomers (Figures 10S–11S, SI). At this temperature, short-lived TC species cannot be followed in the NMR time scale. Yet, they were detected at 228 K (Figure 13S, SI). At PSS, the conversion ratio from the closed form to the open form was 40%, comprising 26% of TTT and 14% of CTT. The conversion ratio is rather low. The chemical shifts of protons in TTT and CTT are very similar, except those belonging to the anisole and phenyl group at the 3-position and in particular H2' and H2'' protons of interest (Table 1S, Figure 13S, SI). For instance, H2' (6.57 ppm) in TTT is upfield compared to H2' (7.24 ppm) in CTT. For H2'', a reverse scenario is observed. H2'' (6.69 ppm) in CTT is upfield compared to H2'' (7.32 ppm) in TTT. As in CTT for **1**, H2' and H2'' in TTT and CTT respectively interact in edge-to-face fashion with the phenyl group of the carbazole unit. To gain more information about the effect of these CH– $\pi$  bonds in the energy difference between all isomers, we carried out DFT calculations. CF2 is the most thermodynamically stable isomer (Figure 3). More importantly, due to the CH– $\pi$  bond, TT isomers becomes more thermodynamically stable than their TC counterparts. In the reference compound displaying T-type photochromism, a reverse scenario is observed in which TC is the most stable open isomer. This finding indicates that P-type photochromic naphthopyrans are obtained for compounds in which TT isomers are the most stable open isomers. In **2**, this has been possible due to the stabilizing energy through intramolecular CH– $\pi$  bonds in TT isomers that counterbalances in some way the stabilizing energy of the CH–O bond in TC isomers.

In conclusion, we showed for the first time that [3H]-naphthopyrans can display unusual inverse- or P-type photochromism through the manipulation of relative thermodynamic stabilities of open isomers with CH– $\pi$  bonds. The relative energy of all isomers is an important parameter that should be taken into account in the design of naphthopyrans with specific properties.<sup>13</sup> P-type photochromic naphthopyrans rely on the introduction of fused rings in the k-face. Such photoswitchable molecules with improved properties could be an interesting alternative to azomolecules in applications requiring among others a large geometry change upon photoisomerization. The modulation of fused (hetero) rings in the k-face of [3H]-naphthopyrans is underway in our laboratory.

**Supporting Information Available.** Experimental procedures, spectroscopic data, and DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.

(12) Rosaria, M.; Nunzio, di; Gentili, P. L.; Romani, A.; Favaro, G. *J. Phys. Chem. C* **2010**, *114*, 6123.

(13) Song, L.; Yang, Y.; Zhang, Q.; Tian, H.; Zhu, W. *J. Phys. Chem. B* **2011**, *115*, 14648.