DOI: 10.1002/anie.201006019

Transparent Metal

Absorption-Induced Transparency[**]

James A. Hutchison,[*] Deirdre M. O'Carroll, Tal Schwartz, Cyriaque Genet, and Thomas W. Ebbesen[*]

In the past decade, the field of optics has been stimulated by new concepts such as plasmonics and extraordinary optical transmission, which are paving the way for next-generation photonic components.[1–6] In this context, hybrid materials that combine the properties of structured metals with semiconductor or molecular materials to create novel functionalities offer much potential.[7–11] While studying molecule–metal interactions, we have found a new phenomenon whereby molecules can induce transparency in optically thick metal films perforated with subwavelength holes. Nonintuitively, transparent windows are opened up at wavelengths at which the molecules absorb strongly, that is, where one would normally expect no transmission.

Here we report a detailed study of this phenomenon showing, among other things, that the molecular material must be within the dipole coupling distance (less than ca. 20 nm) from the metal surface, and that the mechanism involves surface plasmons but is independent of the arrangement of the holes. The phenomenon thus provides new flexibility for tailoring extraordinary optical transmission through subwavelength holes and points to new directions for preparing plasmonic hybrid materials for photonics and energy-conversion applications.

Absorption-induced transparency (AIT) is best illustrated by the schematic and spectra in Figure 1. Figure 1 a shows the transmission spectrum of a square array of 100 nm-diameter holes milled by focused ion beam (FIB) in a 200 nm-thick Ag film with a period of 250 nm (black curve). Only the transmission peak associated with the (1,0) surface plasmon (SP) resonance on the glass/metal interface of the hole array is visible at 518 nm.[3] When an approximately 30 nm layer of a J-aggregate of a cyanine compound (2,2′-dimethyl-8-phenyl-5,6,5′,6′-dibenzothiacarbocyanine chloride) is adsorbed on the hole array, its transmission spectrum shows an intense new transmission with a sharp onset at 685 nm (red curve). Figure 1 b shows the absorption spectrum of the cyanine J-aggregate layer (measured as 1−reflection) taken on a unstructured part of the same Ag metal film (black solid curve). A sharp drop in reflection is associated with strong absorption of the molecular layer peaking at 697 nm, which is redshifted by about 7 nm from that on a glass surface. The absorption spectrum taken on the hole array itself is further broadened (dashed curve in Figure 1 b). There is strong overlap between the absorption of the adsorbed cyanine and

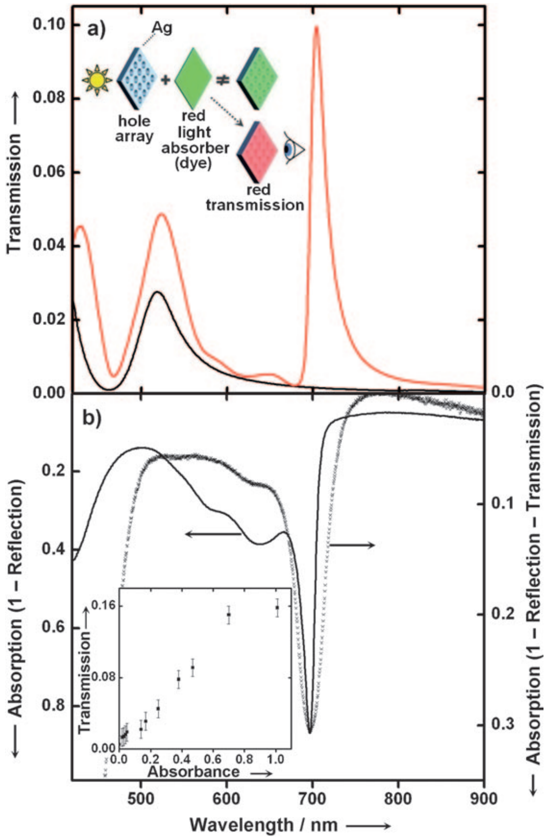

Figure 1. a) Transmission spectra of a square hole array (period 250 nm, hole diameter 100 nm) milled in a 200 nm-thick Ag film in the absence (black curve) and the presence (red curve) of the cyanine J-aggregate. Inset: cartoon depicting the concept of absorption-induced transparency. When a red-light absorber (e.g., a green dye) is adsorbed on an Ag hole array, red-light transmission is observed through the composite. b) Absorption spectrum (calculated as 1−reflection) of the cyanine J-aggregate film recorded at a unstructured part of the metal film (black solid curve), and the absorption spectrum of the J-aggregate recorded directly on a periodic 250 nm hole array (dashed curve), calculated as 1−reflection−transmission). Inset: plot of the transmission peak intensity versus the peak absorbance of the cyanine layer. The J-aggregate was spin-coated from a concentrated chloroform solution (0.15 wt% weight). In this way, J-aggregate layers of up to 30 ± 5 nm thickness could be deposited, as measured by FIB.

---

[*] Dr. J. A. Hutchison, Dr. D. M. O'Carroll, Dr. T. Schwartz, Dr. C. Genet, Prof. T. W. Ebbesen
ISIS, Université de Strasbourg and CNRS (UMR 7006)
Strasbourg 67000 (France)
Fax: (+33) 3-6885-5118
E-mail: hutchison@unistra.fr
ebbesen@unistra.fr

[**] The discussion and help of Dr. E. Devaux, O. Mahboub, and Dr. F. Przybilla are gratefully acknowledged. This research was made possible with the financial support of the European Research Council (grant no. 227577).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201006019.

the intense anomalous transmission through the array. Nevertheless, as shown in the inset of the Figure 1 b, the stronger the absorbance, the stronger is the transmission, which naturally saturates when approaching 100 %. We have verified that the anomalous transmission is not associated with normal fluorescence of the J-aggregates, which are virtually nonemissive in such close proximity to the metal surface (see Supporting Information). The schematic inset in Figure 1 a summarizes the surprising result that the combination of a red-light absorber (which looks green in transmission to an observer) and a hole array in fact results in red transmission.

To elucidate the mechanism of this nonintuitive result, we explored various parameters. The first key observation is that the molecules must be in very close proximity to the surface. As shown in Figure 2 a, when a similar amount of molecules are dispersed in a 200 nm thick polymer film [poly(vinyl alcohol)] spin-cast on the hole array, the modulation of the transmission is very much reduced. Further experiments in which a spacer layer was used to control the distance between the molecules and the metal surface show that the molecules must be within the first 20 nm of the metal to induce the phenomenon efficiently (Supporting Information). Such distance dependence is characteristic of dipole–dipole interactions, in this case between the molecular dipole and its image dipole induced in the free-electron plasma of the metal. Since transmission by subwavelength hole arrays involves surface plasmons (SPs), we investigated whether AIT is sensitive to the capacity of the metal to support SPs. In Figure 2 b the cases of tungsten and gold are compared, as the dielectric constant of the former in this wavelength range is such that it cannot sustain SPs.[12] The transparency peak is extremely weak in the case of W in comparison to Au (and indeed Ag), that is, SPs play a key role. This is further confirmed by putting the array between two crossed polarizers at 45° to the array axis (Figure 2 c). This configuration eliminates all direct transmission through the holes and allows only light that has coupled to SPs to be transmitted.[13] The peak intensity of the anomalous transmission at 710 nm remains essentially unchanged relative to the periodic SP-resonant peaks of the array, and this again implies that SPs are at the heart of the process.

The nature of the AIT can be further clarified by the dependence of the transmission spectrum on the angle of incident radiation on the array (Figure 3 a) and the corresponding dispersion curves (Figure 3 b). In Figure 3 b the dispersion curves of the same array in the absence of molecules is included for comparison. The AIT peak is clearly nondispersive, characteristic of a localized mode. This local character confirms that the AIT mode cannot be due to the shift of a periodic SP resonance owing to a change in refractive index induced by adsorption of the molecular layer. The evolution of the spectrum with angle shows that localized AIT and periodic SP modes interact as they come into resonance, resulting in anticrossing behavior. In the spectra of Figure 3 a, coherent interaction of the modes results in destructive (minima) and constructive (maxima) interferences at given wavelengths above the holes.[14] Another notable feature of the spectra is the sharpness of the AIT peak at certain angles, such as 28° (see Figure 3 c), with a full width

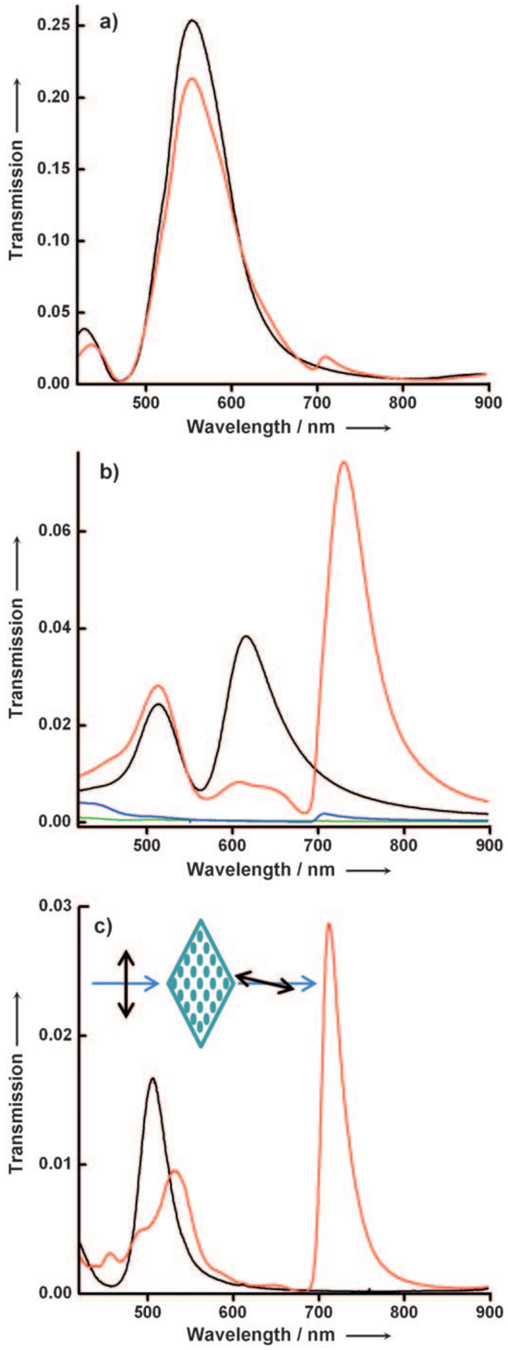

Figure 2. a) Transmission spectra of a square hole array (period: 250 nm, hole diameter: 100 nm, Ag film thickness 200 nm) with a 200 nm-thick poly(vinyl alcohol) film spin-coated on top (black curve) and the same sample with J-aggregates dispersed in the PVA film (red curve). The peak absorbance of the J-aggregate in the film is 0.6. b) Effect of metal. Transmission spectra of square hole arrays (period: 300 nm, diameter 150 nm, film thickness: 200 nm) in the absence (black curve) and presence (red curve) of J-aggregates on Au, and in the absence (green curve) and presence (blue curve) of J-aggregates on W. c) Effect of polarization. Transmission spectra of a square hole array (period: 250 nm, hole diameter: 125 nm, Ag film thickness: 200 nm) recorded with two orthogonal polarizers on either side of the array placed at 45° to the main axis of the array (as indicated by the inset) with (red curve) and without (black curve) cyanine J-aggregates.

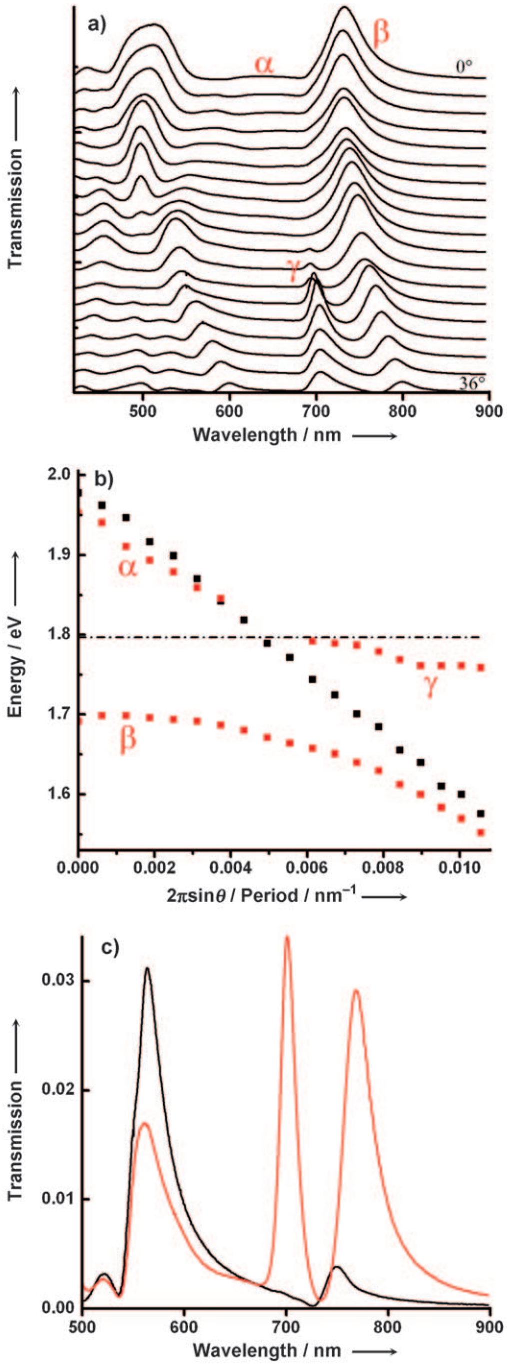

Figure 3. a) Transmission spectrum of a square hole array (period: 350 nm, hole diameter: 100 nm, Ag film thickness: 220 nm) with a J-aggregate film (absorbance: 0.07) recorded as a function of angle of incident radiation. The Greek letters indicate peaks which are plotted in the dispersion curve in Figure 3 b. b) Corresponding dispersion curve showing the details of the interaction between the absorption-induced transmission and the (1,0) SP mode of the periodic structure (red squares). For reference, the dispersion of the (1,0) SP mode in the absence of the J-aggregate is shown (black squares). The dashed line indicates the energy of the J-aggregate absorption peak (see Figure 1 b). c) Transmission spectra recorded at an angle of 28° in the absence (black curve) and presence (red curve) of the J-aggregate. Notice the exceptionally sharp peak at 701 nm.

at half-maximum of only 4 meV. Such sharpening can reflect a large change in damping conditions (increased lifetime),[14] but more detailed studies are required to investigate this issue.

The effect of periodicity and its associated SP transmission peaks can be removed by studying disordered groups of holes in which the holes are sufficiently separated to be uncoupled.[15] Figure 4 compares the spectrum of a disordered group of holes with that of the same structure with a layer of cyanine J-aggregate, and shows an SEM image of a region of the bare structure (inset). The spectrum of the bare structure is broad and featureless due to localized SP modes (black curve).[16] When the dye molecules are adsorbed, a strong transmission peak is present with a sharp onset at 685 nm (red curve), and surprisingly is comparable in intensity and width to that on periodic arrays. The transmission spectra through the disordered group of holes are not angle-dependent in the absence or presence of the molecular layer (see Supporting Information). All of these results further emphasize the localized nature of the AIT mode. Interestingly, in this particular combination, another transparency peak is apparent around 500 nm due to a higher energy absorption band of the molecule.

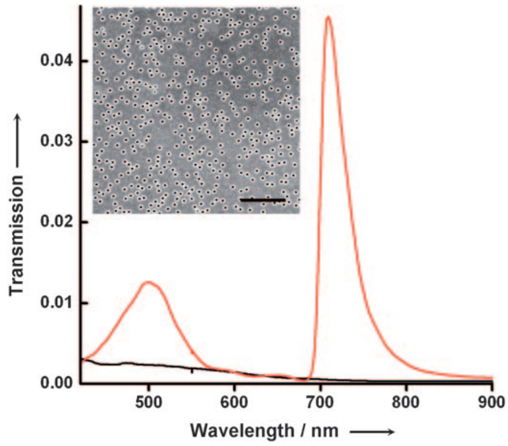

Figure 4. Transmission spectra of a disordered group of holes (hole diameter: 100 nm, minimum hole separation: 100 nm, hole density: 5.8 holes per μm^2, Ag film thickness: 220 nm) recorded in the absence (black curve) and presence (red curve) of the J-aggregates. The peak at 500 nm is the result of absorption of the J-aggregate at short wavelengths (see Figure 1 b). Inset: SEM image of a portion of the structure (scale bar 2 μm).

The above results point to the following mechanism for the absorption-induced transparency. The molecules strongly interact with the free electrons of the metal by a dipole-induced dipole coupling mechanism when placed within the first 20 nm or so of the surface. At these distances molecular excitations are known to be strongly quenched by energy transfer to the metal. As discussed in detail by Barnes,[17] electronic charge density oscillations are induced in the metal with excitation of electron–hole pairs. It has been long assumed that coupling molecular excitations to such lossy surface waves results only in nonradiative damping. While this may be true in the case of molecules placed on smooth metal surfaces, several molecular fluorescence studies have shown that structuring the metal surface (e.g., surface roughness or gratings) provides a path for outcoupling the emission via surface plasmons into the far field.[17–22] In the present study, the small holes have a very broad spectrum in Fourier space that leads to a high density of local photon modes,[17,22] which probably serve to couple the short-distance energy transfer from the excited molecules to SPs. Localized SP modes at the apertures are present in both the periodic arrays and disordered groups of holes, and it is possible that they interact with the molecular resonance to enhance transmission. The holes then play a second role in scattering (or decoupling) these SPs into freely propagating light. This process best explains the strong transmission peak associated with the absorption when the molecules are very close to the metal surface. This mechanism also accounts for the fact that the transmission intensity increases with increasing molecular absorption. The implication of SPs is evident from the enormous difference in the results on W versus Ag or Au and, among other things, the polarization measurements.

Superimposed on this phenomenon is a strong index variation around the molecular absorption peak (Kramer–Krönig relationship). This can be easily seen on optically thin (translucent) metal films covered with dyes, where the transmission is dominated by the real part of the dielectric constant of the molecule.[23] The modulation of the transmission is therefore very similar on metals such as W and Au, unlike in the present case of perforated optically thick films. However the asymmetric line shape of the AIT peak could easily be the result of this index variation and the cutoff function of the apertures. Certainly there is some degree of filling of the holes with molecular materials depending on the conditions (see Supporting Information). Asymmetric line shapes have also been observed for dye molecules adsorbed on metals with localized SP resonances[24] and predicted for energy transfer between a molecule and a metal film by excitation of electron–hole pairs inside the metal.[25] A detailed theoretical study would be necessary to elucidate the possible contributions of the above mechanisms to the observed spectra, which is beyond the scope of the present report.

The AIT peak is unusually intense (see Figures 1 and 4, in which the transmission maximum is boosted by a factor of about 50 compared to the bare arrays). For periodic arrays, it is comparable to the extraordinary optical transmission phenomenon through subwavelength holes,[3,6] while for disordered groups of holes, in which this phenomenon is absent, it occurs with similar intensity. Thus, the AIT is not constrained by periodicity. In effect the phenomenon occurs even for a single hole. Taking the disordered group of holes in Figure 4 as an example, the AIT peak at 708 nm has an absolute transmission of less than 5%. However when normalized to the open area of the structure, the transmission is about 100%. This is surprising, since the molecular film itself absorbs more than 25% of incoming radiation at this wavelength under normal conditions (e.g., if the J-aggregate film were on glass). The intensity of AIT at 708 nm seems even more surprising considering the hole diameter is far below the cutoff wavelength (ca. $\lambda/2$) for efficient transmission. However, the cutoff function of the hole will be altered by partial filling with the dye material and the associated variation in index around the molecular absorption.

In this study we used J-aggregates because of their sharp absorption features, but we have verified that the transparency is independent of the state and nature of the absorber. This opens a new way to tailor the transparency of thick metal films in the visible spectrum and beyond through a simple choice of molecules or any absorber. Instead of changing the nanostructure to control the properties of molecules, it is the molecules that play the major role in determining the properties of the hybrid structure. The close proximity of the molecules to the surface, combined with the scattering structures, engineers the extraction of energy that otherwise would have been lost in the metal, and shows the potential of such hybrid materials for energy-conversion applications. In addition, molecules can provide unique functionalities which can be used to induce permanent or transient changes in the hybrid material. For instance, ultrafast optical switches or filtering gates can be simply made by combining the metallic structure with an appropriate dye.[7] The energy-transfer process from molecules to SPs in the AIT hints at an efficient way to induce strong coupling[26,27] and thereby offers yet another means to control the properties of both the molecules and the SPs of the hybrid structure. The phenomenon is by no means limited to molecules; any oscillating dipole (atoms, quantum particles, etc.) will do. It thus opens new avenues for building plasmonic materials.

Received: September 25, 2010

Keywords: absorption · cyanines · plasmons · optical transmission · transparency

---

[1] W. L. Barnes, A. Dereux, T. W. Ebbesen, *Nature* **2003**, *424*, 824–830.

[2] A. V. Zayats, I. I. Smolyaninov, A. A. Maradudin, *Phys. Rep.* **2005**, *408*, 131–314.

[3] C. Genet, T. W. Ebbesen, *Nature* **2007**, *445*, 39–46.

[4] Z. Liu, H. Lee, Y. Xiong, C. Sun, X. Zhang, *Science* **2007**, *315*, 1686.

[5] G. Noy, A. Ophir, Y. Selzer, *Angew. Chem.* **2010**, *122*, 5870–5872; *Angew. Chem. Int. Ed.* **2010**, *49*, 5734–5736.

[6] T. W. Ebbesen, H. J. Lezec, H. F. Ghaemi, T. Thio, P. A. Wolff, *Nature* **1998**, *391*, 667–669.

[7] J. Dintinger, I. Robel, P. V. Kamat, C. Genet, T. W. Ebbesen, *Adv. Mater.* **2006**, *18*, 1645–1648.

[8] W. J. Padilla, A. J. Taylor, C. Highstrete, M. Lee, R. D. Averitt, *Phys. Rev. Lett.* **2006**, *96*, 107401.

[9] A. Degiron, J. J. Mock, D. R. Smith, *Opt. Express* **2007**, *15*, 1115–1127.

[10] H.-T. Chen, J. F. O'Hara, A. K. Azad, A. J. Taylor, R. D. Averitt, D. B. Shrekenhamer, W. J. Padilla, *Nat. Photonics* **2008**, *2*, 295–298.

[11] P. Vasa, R. Pomraenke, S. Schwieger, Yu. I. Mazur, V. Kunets, P. Srinivasan, E. Johnson, J. E. Kihm, D. S. Kim, E. Runge, G. Salamo, C. Lienau, *Phys. Rev. Lett.* **2008**, *101*, 116801.

[12] F. Przybilla, A. Degiron, J.-Y. Laluet, C. Genet, T. W. Ebbesen, *J. Opt. A* **2006**, *8*, 458–463.
[13] K. A. Tetz, L. Pang, Y. Fainman, *Opt. Lett.* **2006**, *31*, 1528–1530.
[14] C. Ropers, D. J. Park, G. Stibenz, G. Steinmeyer, J. Kim, D. S. Kim, C. Lienau, *Phys. Rev. Lett.* **2005**, *94*, 113901.
[15] F. Przybilla, PhD. Thesis, Université de Strasbourg, **2009**.
[16] A. Degiron, H. J. Lezec, N. Yamamoto, T. W. Ebbesen, *Opt. Commun.* **2004**, *239*, 61–66.
[17] W. L. Barnes, *J. Mod. Opt.* **1998**, *45*, 661–699.
[18] J. R. Lakowicz, *Anal. Biochem.* **2005**, *337*, 171–194.
[19] W. Knoll, M. R. Philpott, J. D. Swalen, A. Girlando, *J. Chem. Phys.* **1981**, *75*, 4795–4799.
[20] S. C. Kitson, W. L. Barnes, J. R. Sambles, *Opt. Commun.* **1996**, *122*, 147–154.
[21] R. W. Gruhlke, D. G. Hall, *Appl. Phys. Lett.* **1988**, *53*, 1041–1042.
[22] J. H. Kim, P. J. Moyer, *Appl. Phys. Lett.* **2007**, *90*, 131111.
[23] E. G. Bortchagovsky, U. C. Fischer, *J. Chem. Phys.* **2002**, *117*, 5384–5392.
[24] H. G. Craighead, A. M. Glass, *Opt. Lett.* **1981**, *6*, 248–250.
[25] D. C. Langreth, *Phys. Rev. Lett.* **1985**, *54*, 126–129.
[26] J. Dintinger, S. Klein, F. Bustos, W. L. Barnes, T. W. Ebbesen, *Phys. Rev. B* **2005**, *71*, 035424.
[27] A. Salomon, C. Genet, T. W. Ebbesen, *Angew. Chem.* **2009**, *121*, 8904–8907; *Angew. Chem. Int. Ed.* **2009**, *48*, 8748–8751.