Photoresponsive Materials

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Controlling the Emission Polarization from Single Crystals Using Light: Towards Photopolic Materials**

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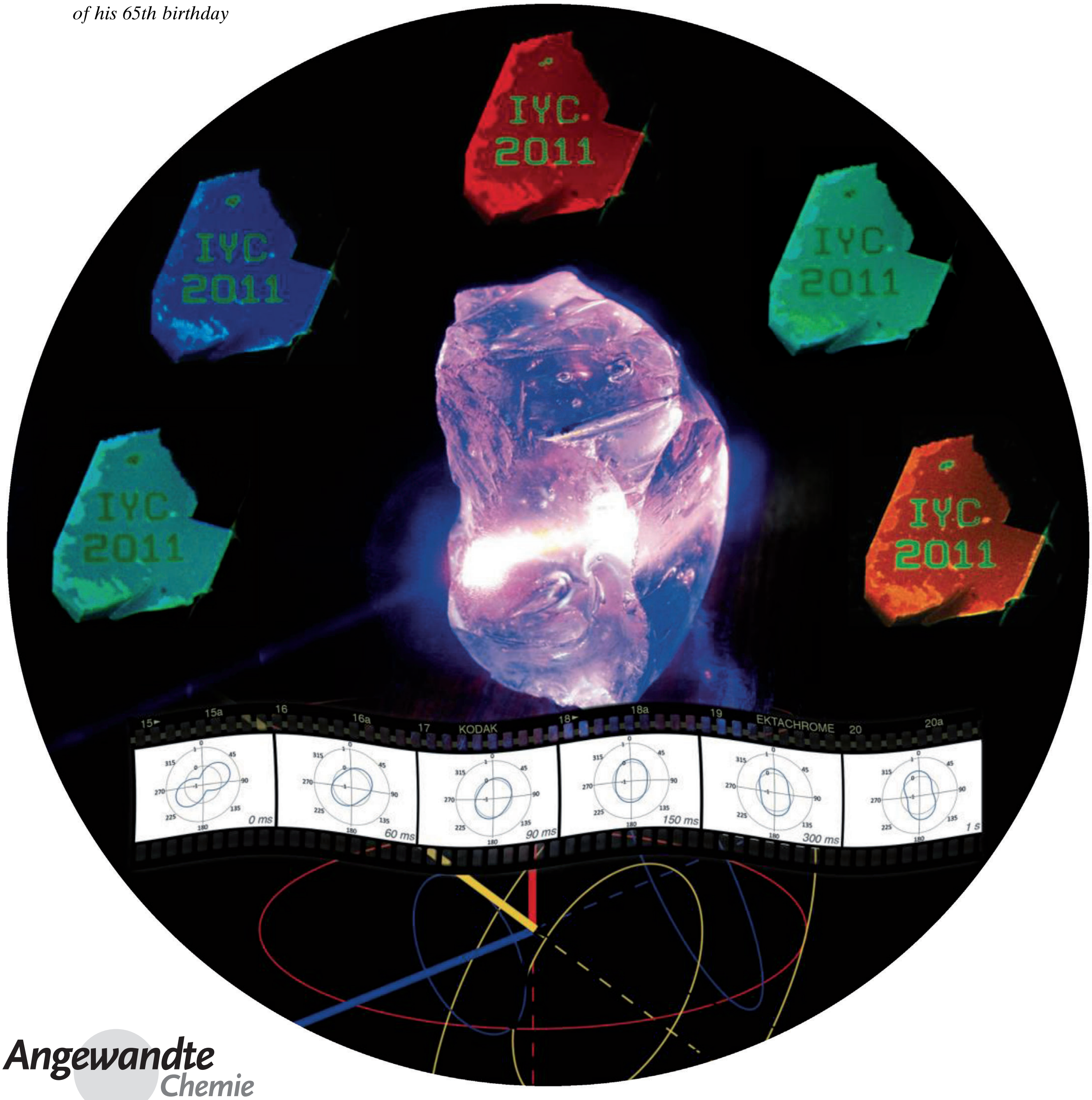
Dedicated to Dr. J.-P. Desvergne on the occasion of his 65th birthday



The use of light to inscribe information has greatly impacted modern technology, which relies on photolithographic techniques for device fabrication and information storage.[1] Photosensitive materials displaying properties that can be controlled and/or probed using light have thus played a tremendous role in the technological revolution, with current read/write processes relying on variations in intensity (amplitude modulation) or energy (frequency modulation) to transfer information to and from substrates.[2] However, the orientation of the magnetic and electronic field vectors of a light beam define a third property of light, its polarization, whose use in lithographic applications has remained largely unexplored caused by the lack of suitable materials. Polarized light can be used, for example, to address chiroptical functionality,[3] or to select chromophores whose electronic transition dipole moments are aligned with the excitation beam and induce their bulk transport in soft liquid crystalline[4] or polymeric materials.[5]

Although the vast majority of luminescent compounds will emit polarized light when suitably aligned (e.g. in crystalline samples or embedded in anisotropic hosts), there is as yet no example of a material whose polarization can be durably and predictably switched using an external light stimulus. By analogy with photochromic materials,[6] whose absorption spectrum can be changed using light, such materials would be termed photopolic (from the Greek πόλωση, polarization). We now report such a material, based on a fullerene derivative that forms organized supramolecular wires in the solid. Regardless of the polarization of the incident radiation, the light emitted is polarized along a specific molecular axis of the crystal. Upon irradiation, the polarization of the emitted light undergoes a rotation of ca. 70° with respect to its initial orientation without any significant changes in its emission profile, intensity, or excited-state lifetime. No detectable loss, transport, or gain of material is observed during the writing procedure. Herein, we show that this process can be used to write optical information onto the material, which can be read through the polarization component of the luminescence emitted by the material. This approach represents a new entry in the photocontrol of light–matter interactions and opens up new perspectives for the fabrication of photonic materials.

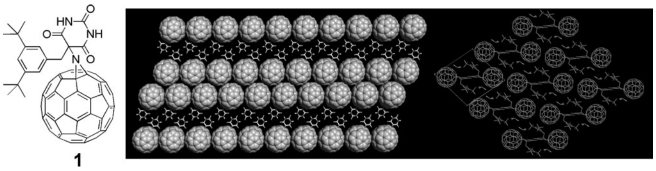


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Figure 1. Chemical structure of compound **1** and solid state structure highlighting the formation of H-B ribbons. Solvent and aromatic residues removed for clarity (on center image only).

Since their discovery, fullerenes have sparked interest as *n*-type semiconductor materials in organic field effect transistors[7] or organic photovoltaic cells.[8] The design of supramolecular fullerene architectures based on hydrogen-bonding (H-B) interactions has proven interesting for further tuning the properties of fullerene materials.[9] We designed compound **1** (Figure 1) as a soluble fullerene derivative that possesses multiple H-B donor–acceptor sites that can be used as reversible points of attachment in the construction of noncovalent supramolecular architectures.[10] We further showed that, in the solid, **1** spontaneously forms fullerene cables, in which interfullerene electronic interactions are highly oriented, as evidenced by the strongly polarized photoluminescence from single crystals. The polarization (p) of the emission and its dependence on the crystal orientation $p(\theta)$ can be quantified according to Equations (1) and (2):

$$p = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} \tag{1}$$

$$p(\theta) = a\sin(\omega(\theta + \varphi)) + c \tag{2}$$

where $I_{\parallel}$ and $I_{\perp}$ are the fluorescence emission intensity components oriented parallel and perpendicular to the polarization of the excitation beam, respectively, corrected for instrumental response but not for the depolarization effects of the large numerical aperture objective.[11] Equation (2) represents an approximation of a single dipole oscillator model in which a, c, ω, and ϕ, are the maximum amplitude, offset, period, and phase of the polarization with respect to the macroscopic orientation of the crystal.[12] In the case of **1**, the maximum observed value of p (0.78) is very large, clearly indicating that the emission is highly oriented along a specific direction of the molecular crystal.[10]

While investigating the luminescence properties of crystals of **1**,[13] we noticed that the polarization of the samples would change upon irradiation, suggesting a photoreaction. However, this change is not accompanied by a substantial decrease in the intensity of the fluorescence emission from the sample (Figure 2a). Simultaneous monitoring of the parallel and perpendicular components of the emission reveals that the decrease in one channel is compensated by the increase in the intensity detected at the other channel (Figure 2c). This behavior is indicative of an alteration of the emitting chromophore that, surprisingly, is not accompanied by a significant change in the emission spectra (Figure 2d), or in the average fluorescence decay time of the excited state, which undergoes a small increase upon irradiation (from 1.17 ns to 1.20 ns). Thus, the new emission is also polarized, with a maximum value of $p = 0.42$ that is rotated with respect to the direction of the initial emission polarization. The rotation corresponds to a change in the phase of the angular dependence of p, which is relatively constant from crystal to crystal and centered around $\Delta\phi \approx 70°$,[14] as can be seen in

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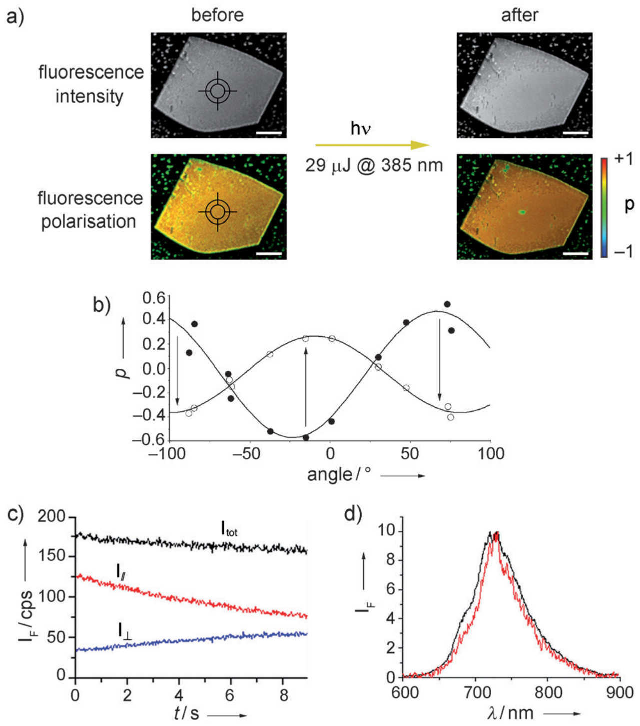

Figure 2. a) Confocal fluorescence microscopy images of the intensity and polarization from a single crystal of **1** before and after being irradiated with a laser beam at the point indicated by the crosshair (scale bar is 10 μm). Only a change in the polarization of the fluorescence emission is observed. b) Graph of p vs. crystal orientation before (filled circles) and after (empty circles) irradiation. Solid lines represent best fit according to Equation (2). Arrows indicate a change in p upon irradiation. c) Variation of the parallel ($I_{\parallel}$) and the perpendicular ($I_{\perp}$) components of the total fluorescence emission (I_{tot}) collected at the laser spot during irradiation of the sample in A. d) Fluorescence emission spectra (uncorrected) collected from an area on the surface of a single crystal of **1** before (black line) and after (red line) irradiation.

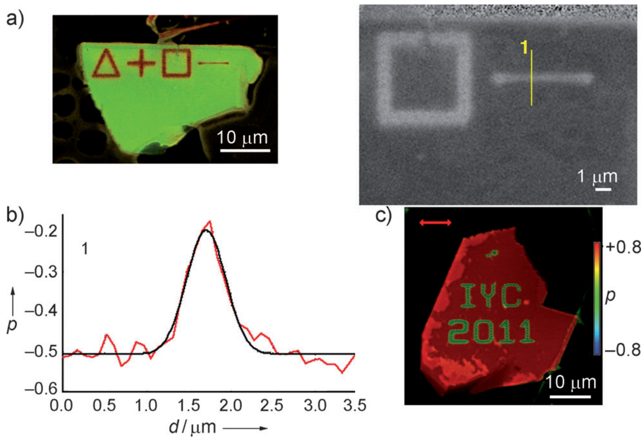

Figure 3. a) Examples of polarization-based lithography. The triangle, plus sign and square were obtained by irradiating overlapping points, whereas the single line was obtained by scanning the laser beam (fluorescence polarization image). Close-up of the square and line patterns is shown on the right. b) In the case of line 1, a Gaussian profile (fwhm = 435 nm, black line) is observed. c) A short text commemorating the UNESCO International Year of Chemistry 2011 was written on a single crystal (the red double arrow shows the polarization of the excitation beam). Emission polarizations for other crystal orientations are shown in Figure S3.

Figure 2b, where values of p before and after irradiation are collected for different crystal orientations. Because the orientation of the crystal axes could not be determined unambiguously for each crystal, we define the orientation of the emission polarization with respect to one of the crystal edges. The polarization of the emitted light is therefore experimentally determined by rotating the crystal and plotting the corresponding polar graphs as shown in Figure 2b. Given that the polarization of the emission is systematically rotated, and that this rotation occurs homogeneously over the entire surface that is irradiated, we conclude that the switch in polarization does not originate from random defects in the crystal lattice but from a change in the molecular structure of the material. Furthermore, no differences in the writing process were observed between using an air or an Ar blanket, indicating that it is not dependent upon the presence of oxygen.[15]

By scanning the excitation beam, it is possible to selectively trigger a variation in the emission polarization over a desired area, in a process that is analogous to writing in conventional photolithography (Figure 3). The resolution of the overall process is limited by the diffraction limit of the light that is emitted from the sample, which extends to 800 nm. Consistent with this observation, a full-width-half-maximum of 435 nm is determined for the horizontal line written by scanning the excitation beam back and forth (Figure 3b, line 1).

The results of a kinetic analysis of the writing process for different orientations (θ) of the sample with respect to the excitation beam are summarized in Figure 4. The data was obtained by writing a series of lines onto a single crystal while varying the macroscopic orientation of the crystal with respect to the orientation of the polarized excitation beam. For each orientation, a line was repeatedly written 200 times while simultaneously collecting $I_{\parallel}$ and $I_{\perp}$.[16] The data was treated according to Equation (1) to give a 2D map of p vs. time and position along the line. The data along each line was then averaged to form graphs of p_{av} vs. time collected for different crystal orientations (θ) (see Figure S4). The results indicate that the writing is insensitive to the polarization of the excitation beam, and that the initial and final polarization of the emission only depend on the orientation of the substrate with respect to the analysis polarizer. Moreover, p_{av} values obtained at different angles θ were fitted according to Equation (2) to generate polar graphs of $p(\theta)$ vs. irradiation time (Figure 4a), whereas the resulting phase and amplitude values vs. irradiation time are plotted in Figure 4b.

The energy required for the writing is roughly fifty times higher than that used for imaging, which can be attained either using slower scan speeds or higher beam intensities (Figure S1), thus suggesting that the process depends on the total irradiation and not the photon flux. To further exclude that the variation in polarization could be caused by localized heating during the writing procedure, a chopper was inserted between the excitation source and the sample.[17] Variations in the chopper speed had no effect on the resulting polarization

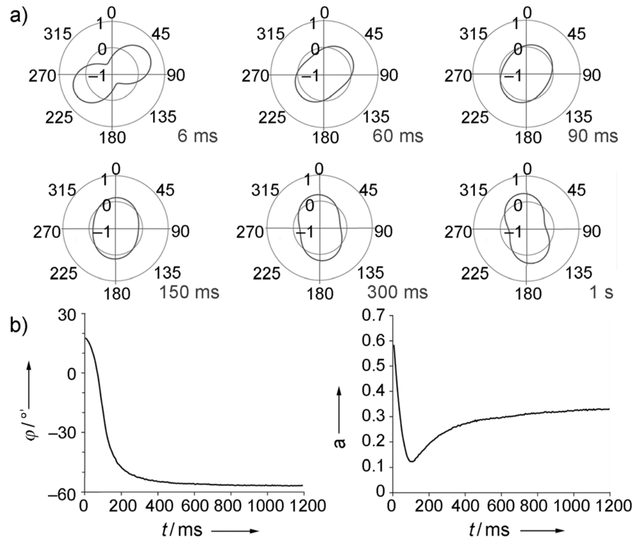

Figure 4. The kinetic rates of the photoinduced rotation of the fluorescence polarization were probed by writing a series of lines on a single crystal of **1**. a) Polar graphs p_{av} vs. θ obtained by fitting the experimental data at 6, 60, 90, 150, 300, and 1000 ms according to Equation (2). b) Phase (ϕ) and amplitude (a) of the polarization as a function of irradiation time, as extracted from 200 polar graphs with 6 ms $< t <$ 1.2 s ($\Delta t = 6$ ms). See Figure S4 and Table S1 for the kinetic analysis of individual lines.

component, and identical plots of p vs. E_{tot} (where E_{tot} is the total incident energy) were obtained for all chopper speeds (see Figure S2). The thermal stability of the samples was probed by placing crystals that were irradiated on a portion of their surface in a heated oven (under inert atmosphere) for a period of time before re-examining the fluorescence polarization. Heating for 30 min at 110 °C had no effect on the polarization of the emission, and the surface could be photopatterned normally. However, heating to 205 °C for 50 min caused a decrease in the polarization of the sample, along with some deterioration of the crystal.

The origin of the photoinduced switch of the emission polarization may be understood on the basis of the spectroscopic properties and supramolecular structure of the material. It is expected that the spherical symmetry of fullerene precludes any anisotropy in the electronic transition dipole moments. This is presumably the case (or nearly so) for the absorption by crystals of **1**, in agreement with the non-dependence of the fluorescence emission intensity on the polarization of the excitation beam.[18] The fluorescence emission from single crystals of **1** is considerably red-shifted with respect to fluid solution, and has been previously attributed to emission from excimer-like emitting states in analogy with the emission from solid samples of fullerene C_{60}, in which the electronic excitation energy is delocalized over two fullerene chromophores.[10,19] Thus, in contrast to the absorption of photons which occurs on a single chromophore, the emission originates from the interaction of several chromophores and can therefore be polarized.[20] In the case of single crystals of **1**, strong anisotropy can be expected because of the formation of hydrogen-bonded fullerene ribbons, which is consistent with the observation of strongly polarized excimer-like emission. Fullerenes are also well known to undergo photoinduced [2+2] cyclodimerization across the 6,6 C=C bonds in the solid[21] or in solution when maintained in close proximity using covalent[22] or supramolecular interactions.[23] We assign the initially polarized emission to originate from fullerene excimer-like emitting states that are photoreactive. In this model, continued irradiation will eventually lead to dimerization of these lowest-energy excimer-like emitting states, which raises their energy above that of other excimer-like states.[24] This raise in energy would eventually lead to the population of the next-lowest lying excited state, localized on a different excimer-like emitting state, whose emission dipole moment is oriented differently from the first.

In summary, we have shown that the correct alignment of photoreactive chromophores can lead to materials in which the emission of polarized light can be controlled in a predictable fashion without relying on the gain, transport, or loss of material. Such materials, which we term photopolic, may be of interest for optical information processing. In the case of crystalline samples of **1**, the emission polarization is rotated by approximately 70° upon irradiation using polarized or nonpolarized light, and this compound represents the first example of a material whose emission polarization can be controlled without altering its emission frequency or intensity. Contrary to the fluorescence of fullerenes in solution, the emission from the crystalline samples of **1** is easily detected and may make this material interesting for the design of photonic devices operating in the near infrared.

Experimental Section

Sample preparation: The samples are prepared by drop casting the solution containing the crystals directly on the microscope cover glass, and by letting it dry under ambient conditions.

Microscopy: Measurements are performed on a Picoquant Microtime 200 inverted confocal microscope, using a PicoHarp 300 multichannel single-photon counter and two MPD SPADs. The excitation originates from a frequency-doubled Ti–sapphire laser (Coherent) tuned at 385 nm with picosecond pulses (4–6 ps) at 4.76 MHZ repetition rate. The laser beam is coupled to a polarization-maintaining single-mode fiber optic, collimated and finally injected by 90° reflection on a 80 %T/20 %R spectrally flat beam splitter into the microscope oil immersion objective (100 × UPLSAPO, N.A. 1.4). The control of excitation light polarization is obtained with a Babinet Soleil compensator. The emission is collected by transmission through the same beam splitter and a 470 nm long-pass interferential filter before being focused on a 50 μm pinhole. Parallel and perpendicular components of the emitted light are split using a polarizing beam splitter and two Glan-Thompson polarizers. The instrumental G-factor is measured for the emission spectrum of **1** itself, by choosing a reference crystal and taking successively two acquisitions between which both the linear excitation polarization and the sample were rotated by 90°. The G-factor is then given by the relation $G = ((I_V/I_H)_{0°} * (I_V/I_H)_{90°})^{1/2}$, where I_H and I_V are the intensities of the horizontal and vertical components of the fluorescence emission, respectively. Total fluorescence intensity was determined according to $I_{tot} = I_{\parallel} + 2GI_{\perp}$. For emission micro-spectroscopy measurements, after the pinhole, light is diverted into an Andor SR300i spectrometer equipped with a Newton EMCCD.

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[13] Single crystals of **1** were grown by the slow diffusion of chloroform into an *o*-dichlorobenzene solution of **1** and belong to the triclinic space group ($P\bar{1}$) with cell parameters $C_{79}H_{25}N_3O_3{\cdot}CHCl_3$, $a = 9.952(2)$ Å, $b = 15.876(3)$ Å, $c = 15.877(3)$ Å, $\alpha = 77.41(3)°$ $\beta = 83.69(3)°$ $\gamma = 88.42(3)$. For more information, see ref. [10].

[14] Although the crystals lie reasonably flat on the substrate, the value of $\Delta\phi$ will also depend on the tilt angle of the crystal with respect to the substrate.

[15] Bleaching of the fluorescence emission was observed to be faster in the presence of oxygen.

[16] During a writing cycle, each point in the line is irradiated for 6 ms, for a total of 1.2 s/line at an incident laser power of 1.4 μW (4.4 $\mathrm{kW\,cm^{-2}}$), with points separated by a distance of 100 nm.

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