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NIR photoresponse in the mixed phthalocyanine films

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Abstract: The structure, optical and conducting properties of thin vacuum deposited films of erbium bisphthalocyanine (Pc_2Er) and its mixtures with metal-free phthalocyanine (H_2Pc) have been studied with particular reference to the near infrared (NIR). It has been found that, in spite of intense optical absorbance over the UV/Vis/NIR domain, pure Pc_2Er films are weakly photoconductive. However, in the mixed Pc_2Er/H_2Pc films the photocurrent signal was detected in the NIR range of 1200-1500 nm, which is associated with optical activity of Pc_2Er molecules.

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1 Introduction

Bis-phthalocyanines of the rare earth metal group (Pc_2RE) have been known for decades [1] as an important class of porphyrin-like compounds. The double-decker molecular architecture (Fig. 1) determines peculiarities of the crystal structure [2–8] and conducting properties of the Pc_2RE solids [2, 7, 9–12], which differ substantially from the conventional (mono-) metallophthalocyanines, MPc.

In optical spectra the differences are not so pronounced. Nevertheless, sublimed films of Pc_2RE in neutral form exhibit a broad absorption band (multiplet) of moderate intensity in the near infra-red, at *ca.* 1300-1600 nm (position depends slightly on the RE atom), where MPc do not have any noticeable absorption[†] [2, 5, 7, 13–15]. Such spec-

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[†] This should not be confused with very weak absorption bands observed in some transitional metal

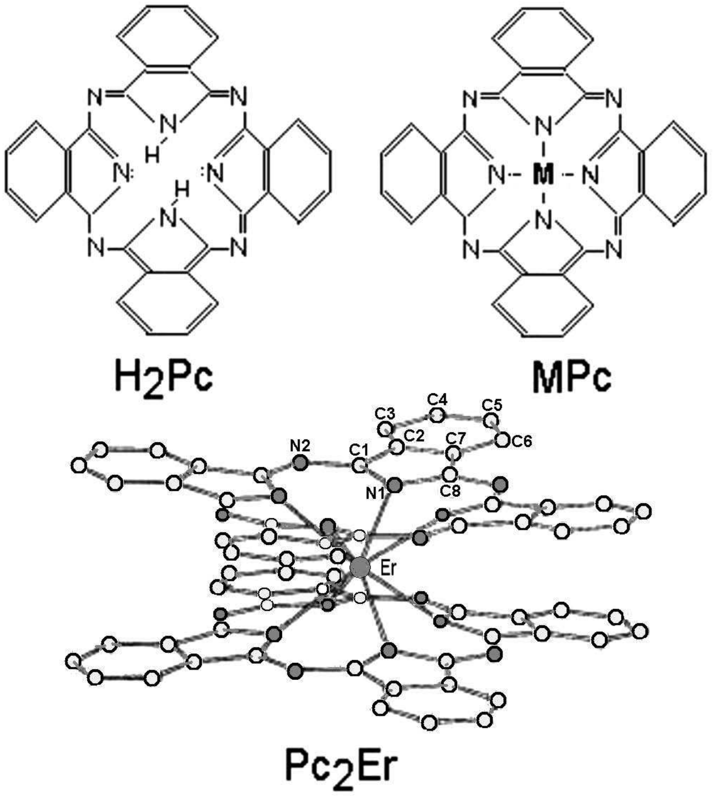

Fig. 1 Molecular structures of phthalocyanines discussed in this work.

tral features are of practical importance, as they coincide with the optical communication wavelengths. Attempts to exploit the electrochromic or gas detecting properties of Pc_2RE in this spectral range were recently made [13].

Solid state Pc_2RE demonstrate intrinsic semiconductivity, their dark electrical properties are described *e.g.*, in Refs. [2, 3, 7–10, 12, 17]. Although typical for MPc absorption bands in the UV/Vis domain, like Soret and Q, corresponding to electronic transitions in the Pc-ligand, also appear in the spectra of Pc_2RE [2, 4, 5, 7, 14, 17], there are seemingly no reports on opto-electronic applications or at least photoconductivity of these materials [11, 17]. This is in a marked contrast to MPc. In this paper we describe some optical and electrical measurements on thin films based on (bis-phthalocyaninato-)erbium (Pc_2Er), with focus on the NIR domain.

2 Experimental

The target compound, Pc_2Er was synthesized and purified as described earlier [18]. Thin polycrystalline films were prepared by a thermal evaporation in high vacuum (VUP-5 SU installation) on various substrates. The samples were characterized by X-ray diffraction

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phthalocyanines (CuPc, PbPc) around 1000-1300 nm, which are due to the forbidden S0-T1 electronic transitions. This leads to direct creation of the long-lived triplet excitons giving rise to photostimulated current [16].

(DRON-4M diffractometer, CuKα radiation), atomic force microscopy (Solver P4), FT-IR spectroscopy (InfraLum FT-02) and UV/Vis/NIR spectroscopy. In the latter case, a MDR-41 LOMO monochromator (equipped with KS-13 or GaAs optical filters in order to remove additional diffraction) was coupled to a 150W halogen lamp and calibrated Si- or Ge- photodetectors, all interfaced with a computer. The same experimental setup was used for photocurrent measurements. The data presented below were acquired with a 1 kHz chopper modulation using a Unipan lock-in nanovoltmeter type 232B.

Two types of cells were fabricated for (photo-)electrical measurements: i) insulating supports with interdigitated contacts (various metals), and ii) sandwich heterostructures "glass/ITO/Pc_2Er/Metal" with effective area *ca.* 1 mm^2. Current *vs.* voltage and *vs.* temperature characteristics were recorded. The obtained Pc_2Er films exhibited low, relative to MPc, bulk resistance in the range of few kOhms (*cf.* – [9]), therefore, observation of a reliable photoeffect in the sandwich cells was difficult. Hence, the films deposited on the Sitall[‡] substrates with lithographically patterned Ni contacts will be considered here (raster parameters are: finger length 3 mm and width 0.03 mm, interfinger distance 0.03 mm, number of pairs 30 and height of metallization 200 nm). For these, the space charge limited currents (power coefficient similar to 2) were observed in the range of 0.2-20 V, and thermal activation energy of 0.33 eV in this regime was derived – *cf.* [2, 10].

3 Results and discussion

Both UV/Vis/NIR and FT-IR spectra indicate that molecular structure of the double-decker compound was not damaged during the sublimation, and the films are composed of neutral "green" radical form of Pc_2Er (cf. – [4, 5, 7, 14, 19]).

The film surface has a hill-like topology with densely packed rounded grains, which is common for thin sublimed MPc layers. The average grain diameter of 100-150 nm and height of 30-40 nm was measured, with RMS roughness about 17 nm, *cf.* – [12].

In Fig. 2 the XRD pattern for the Pc_2Er film evaporated on glass slides (similar to those used for optical measurements) kept at room temperature is shown. As follows from comparison with the literature [2–4, 6], the obtained films are mainly polycrystalline and composed of tetragonal, so-called α-phase, with prevailing orientation of molecular stacks parallel to the surface plane [5, 12]. It should be mentioned that the crystalline structure of the film depends on the substrate materials: the layers grown on the regular surfaces (*e.g.*, Si(111)) have more distinct XRD patterns.

Photovoltaic activity of 36 tetrapyrrole compounds including variously substituted MPc and Pc_2RE was investigated in [11], and no effect was found for the double-decker complexes. The authors attributed this to a "steric" reason: ultimate form of axial coordination (*i.e.*, with Pc-ring instead of halogen atoms or groups) closes the metal atom and hinders the photostimulated charge transfer along the molecular stacks [11].

[‡] Finely polished crystalline ceramic material, Russian analog of Zerodur®, with ultra low thermal expansion and conductance, used mostly as dielectric substrates for electrical measurements and in lithography.

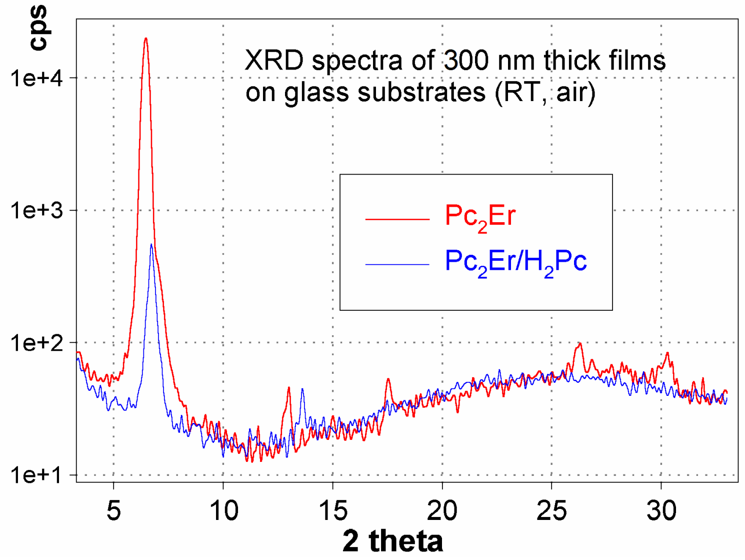

Fig. 2 (color online) XRD spectra of 300 nm thick films of pure Pc_2Er and co-sublimed Pc_2Er/H_2Pc mixture (molecular ratio 1/3).

Indeed, as our preliminary experiments showed, even after exposure to the non-monochromatized light of the tungsten lamp with the water/glass filter the visual rise of current at constant bias was not revealed in the Pc_2Er samples. Yet, the excellent stability of electrical signal (which is quite different from poorly conductive MPc) allows the measurements of very small relative changes in conductivity, and a weak (and slow) photoresponse was eventually detected when using a powerful light source. It is illustrated in Fig. 3A for 300 nm thick Pc_2Er film under cyclic illumination from the top surface. The light from a glowbar lamp (IKS-29 LOMO) was passed through filters, 0.4 mm Si plate + ITO/glass slide, in order to select the optical window approximately from 1000 to 5000 nm and avoid direct heating of samples. Inclusion of the visible range results only in a slight increase of the photoresponse amplitude.

Two assumptions for such a minor effect can be made. First, the concentration of intrinsic charge carriers (holes [2]) in Pc_2RE is high enough, hence the contribution of the photogenerated ones is negligible. Note that the molar extinction coefficients in the UV/Vis domain are typically very high both for MPc and Pc_2RE, hence a large portion of light is being retained by a thin film. Second, the photons absorbed by Pc_2Er molecules do not directly give rise to the photocurrent. Presumably, due to the distinction of molecular packing of Pc_2RE [2–8] the created excited states experience other nonradiative relaxation pathways[§] than those leading to appearance of new, or release of trapped, carriers. These would be some intermolecular (*e.g.*, vibrational relaxation) or intramolecular (*e.g.*, exciton-phonon scattering) processes. In any case, an optothermal conversion will dominate. And indeed, the kinetics of photoresponse (Fig. 3A) closely resembles that caused by the short heat pulses applied to the cell using resistive heating or IR lamp. The experiments on quantitative fixing of the photothermal activation of

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[§] No photoluminescence from Pc_2Er films at various excitations was detected.

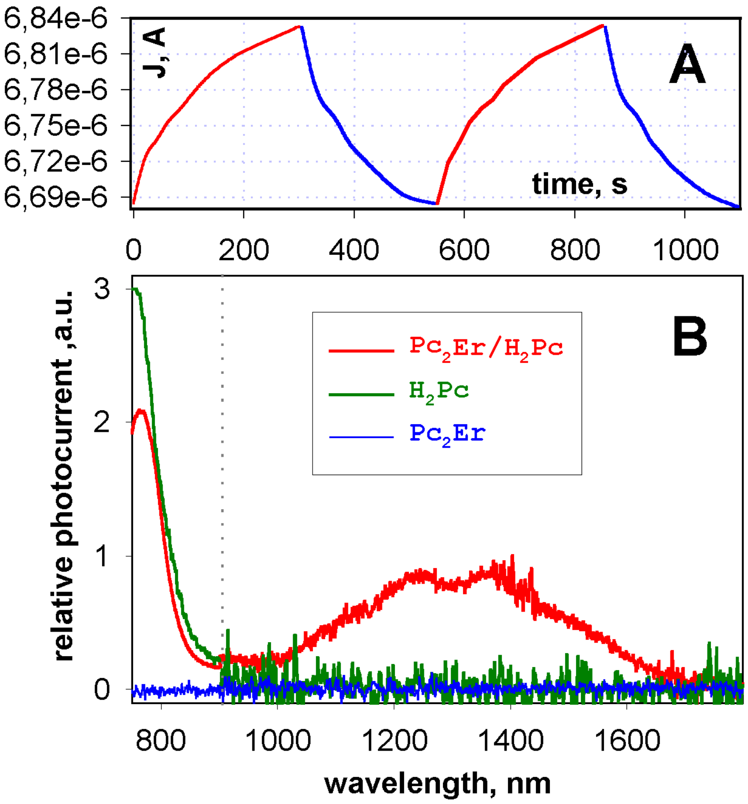

Fig. 3 (color online) A) Photocurrent kinetics at 1V dc (see, text) measured with a HY1802D source and a U5-11 amplifier in a common two-terminal scheme;
B) photocurrent action spectra in the NIR range for phthalocyanine films i) Pc_2Er, ii) Pc_2Er/H_2Pc (1/3) and iii) H_2Pc at 10 V dc. For convenience, the NIR parts of are multiplied by a factor of 3. The data are plotted accounting for the spectral function of lighter.

conductivity in the phthalocyanine thin films are underway.

We are, however, interested in the fast responses in the NIR range. No electrical signal was detected in the cell containing net Pc_2Er layer – Fig. 3B (blue curve). Varying the registration methods (dc or ac current, capacitance), frequency of modulation (0.1-1 kHz) and cell parameters (film thickness, electrode material and arrangement) yielded no reliable results. In attempt to overcome this problem, the two-component molecular system, in which active Pc_2Er molecules are incorporated in an appropriate matrix, was proposed. Based on antecedent reasoning and selective experiments, a metal-free phthalocyanine, H_2Pc was chosen as a matrix material (Avocado, 98%).

As shown earlier, different MPc can form mixed phases by co-sublimation [20]. The XRD spectrum for co-deposited Pc_2Er/H_2Pc film is shown in Fig. 2. It can be seen that crystalline structure and preferable orientation of molecular stacks are maintained in the mixed film. Pure H_2Pc films of such thickness give very weak XRD peaks due to absence of a heavy metal atom. Also, no marked changes were found in the film relief by AFM.

The visible spectrum of a mixed Pc_2Er/H_2Pc film is shown in Fig. 4A together with

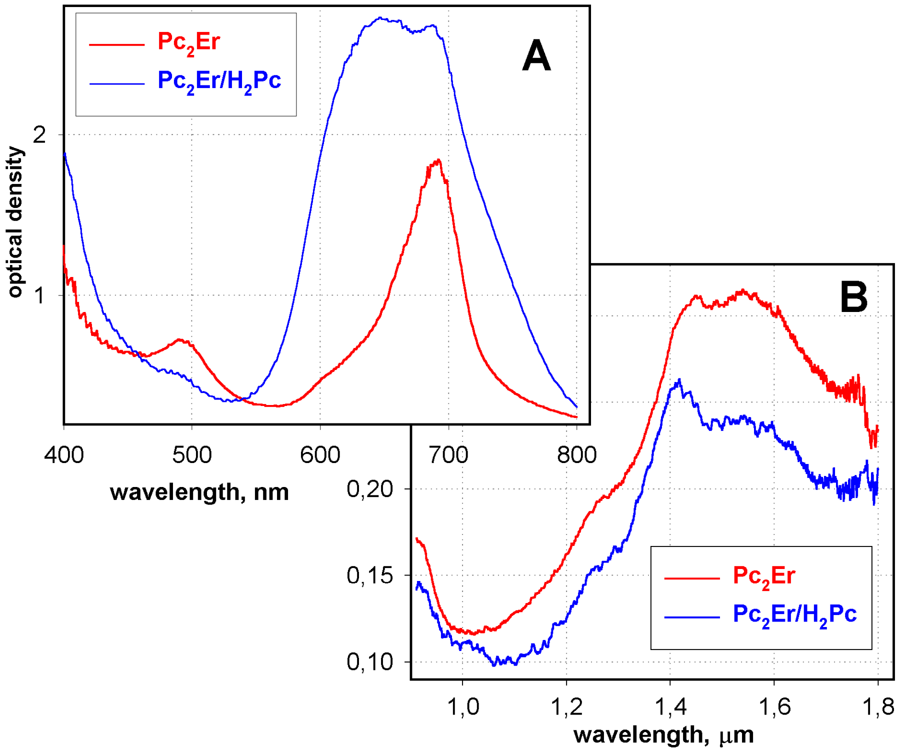

Fig. 4 (color online) Optical absorption spectra in the visible (A) and NIR (B) ranges for a net Pc_2Er, H_2Pc and two-component (as in Fig. 3B) films.

the spectrum of net Pc_2Er film. Regardless of huge Q-band (picked at 630 nm) arising from intrinsic H_2Pc absorption it is clear that the spectral features of bis-phthalocyanine complex (*e.g.*, band near 480 nm pointing to π-radical form of Pc-ring [2, 4, 8, 14–16]) are retained in the two-component system. Moreover, the above-mentioned absorption band in the NIR range remains, – Fig. 4B. It becomes slightly modified as compared to net Pc_2Er (see, Fig. 4B) reflecting possible interaction between the guest and matrix molecules in the Pc_2Er/H_2Pc solid. It is worth noticing that this band itself is very sensitive to chemical environment and vanishes upon oxidation or reduction of neutral Pc_2RE complex.

Furthermore, the specific conductivity of such composite structure is much lower than that of Pc_2Er alone and takes intermediate position with respect to both pure components ($\approx 10^{-8}$ $1/\Omega$cm). Accordingly, the photoeffect in the NIR section of Q-band, which is well known for M(and H_2)Pcs, is now clearly seen in Fig. 3B (left part of the green curve around 850 nm corresponds to a red tail of split Q-band in the absorption spectra).

The NIR photocurrent action spectra of three similarly prepared films: net Pc_2Er, co-evaporated Pc_2Er/H_2Pc (the same as in Fig. 4A,B) and net H_2Pc, are presented in Fig. 3B. As expected, net H_2Pc film gives a huge photocurrent peak going from the red part of visible domain (green curve in Fig. 3B) but is not photosensitive over the entire NIR range. In contrast to the one-component films, the desired signal was obtained in the mixed structure – Fig. 3B, red curve. The shape and position of the photocurrent peak do not completely follow the optical absorption (cf. – Fig. 3B). Two photocurrent maxima are shifted to shorter wavelengths with respect to the basic absorption maximum. The feature at *ca.* 1250 nm apparently conforms to the first short-wave band which is seen as shoulder in Fig. 4B and can easily be picked out by deconvolution of the spectrum. The situation is more complicated at longer wavelengths, it is however clear that the optical absorption here does not determine an increase in photocurrent. This may be connected, for example, with screening effect (as we used the surface cells) or with different contribution of intramolecular electronic transitions forming the multiplet in the photocurrent. The bulk (not junction) nature of the effect was confirmed by varying the contact material and the cell geometry.

4 Conclusions

To our knowledge, this is the first observation of photoassisted conductivity in the phthalocyanine materials at wavelengths longer than 1300 nm. If further amplification is possible, it allows speculation about photodetecting materials based on Pc_2RE in this range. Besides, a certain enhancement of the spectral response of photocurrent in solar cells employing active phthalocyanine layers could be achieved by involving the NIR component [21].

The mechanism underlying this effect merits further investigation (*e.g.*, precise identification of the supramolecular structure and the role of host/guest ratio is needed). The simplest explanation is that the low-energy photoexcited states on Pc_2Er molecules can readily be transferred to (and then transported by) the more resistive H_2Pc matrix, which leads to appearance of a photoinduced current across the layer. However, theoretical studies [14, 15] on the positions of molecular orbitals in individual molecules predict differences in their energies (HOMO and LUMO) much higher than kT[¶]. This means that direct mutual transfer of excited states between these two types of molecules is questionable. If so, other explanations like ionization of impurity levels in the H_2Pc matrix heavily doped with Pc_2Er could be considered.

Acknowledgment

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[¶] In fact, the question of exact attribution of the NIR transitions in Pc_2RE appears to be not completely clear [2, 8, 14, 15], additionally, crystalline effects [8] or RE atom effects [9, 14] may result in deviation from estimated energy levels.

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