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D. Chubich [b], G. Dovbeshko [a], O. Fesenko [a], R. Fedorovich [a], T. Gavrilko [a], V. Cherepanov [a], A. Marchenko [a], A. Naumovets [a], V. Nechitaylo [a], G. Puchkovska [a], L. Viduta [a] & A. Vitukhnovskii [b]

[a] Institute of Physics, National Academy of Sciences of Ukraine, Kyiv, Ukraine

[b] Lebedev Physical Institute, Russian Academy of Sciences, Moscow, Russia

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Light-Emitting Diode of Planar Type Based on Nanocomposites Consisting of Island Au Film and Organic Luminofore $Tb(thd)_3$

D. Chubich[2], G. Dovbeshko[1], O. Fesenko[1], R. Fedorovich[1], T. Gavrilko[1], V. Cherepanov[1], A. Marchenko[1], A. Naumovets[1], V. Nechitaylo[1], G. Puchkovska[1], L. Viduta[1], and A. Vitukhnovskii[2]

[1]Institute of Physics, National Academy of Sciences of Ukraine, Kyiv, Ukraine
[2]Lebedev Physical Institute, Russian Academy of Sciences, Moscow, Russia

Structure, photo-, electroluminescence and electron transport properties of planar nanoscale light-emitting metal-organic device consisting of Au nano-islands and $Tb(thd)_3$ is reported. FTIR and photoluminescence measurements confirm stable vacuum deposition behavior of $Tb(thd)_3$ in a monomeric form. With STM imaging, a thickness-dependent structure of $Tb(thd)_3$ layers was observed and local current-voltage characteristics of organic films were found to be non-linear at voltages exceeding 1.0 V. Electroluminescence from the nanocomposite was observed at voltages 15–30 V, showing the emission features both of $Tb(thd)_3$ and Au nano-islands. The results can be useful for design of planar light-emitting devices with controllable spectral characteristics.

Keywords: electroluminescence; FTIR spectroscopy; photoluminescence; planar nanocomposite; STM; $Tb(thd)_3$ complex

1. INTRODUCTION

Rare earth complexes are promising materials for fabrication of organic electroluminescent devices (OLEDs) due to high efficiency of photoluminescence (PL) and sharp emission bands. In these systems, energy

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Address correspondence to T. Gavrilko, Institute of Physics, National Academy of Sciences of Ukraine, Prospect Nauki, 46, Kyiv 03028, Ukraine. E-mail: gavrilko@iop.kiev.ua

produced by recombination of injected holes (radical cations) and injected electrons (radical anions) excites molecules in an emitting layer. Complexes of lanthanide metal ions such as Eu and Tb have been applied by several researchers as emitting materials in light emitting electroluminescent devices with sharp spectra [1–4]. The sharp emission bands of rare earth ions (the full-width at half maximum of the band is less than 10 nm) are also very suitable for full-color displays. These complexes are easily synthesized and exhibit high-level photoexcited emission. Their PL properties have already been extensively studied, however their quantum efficiency and electroluminescence (EL) performance are still not satisfactory. The efficiency of an OLED strongly depends on the choice of molecules and on the design of device structure. In order to obtain more effective and useful OLEDs using lanthanide-based compounds, we proposed in our recent works [5–7] a new type of planar nanoscale EL device consisting of an island metal film and organic molecules. It is known [8] that when electric current passes through metal nano-islands, they emit electrons and photons capable to provide effective energy transfer to the organic layer. The efficiency of EL from such planar nanoscale devices can be fine-tuned by suitable selection of metals and organics, and to a large extend it depends on molecular organization at the interface between the composite layers.

Here we report on FTIR spectroscopy, photoluminescence and scanning tunneling microscopy (STM) studies of the structure, luminescence properties and electrophysical characteristics of planar nanoscale light-emitting device consisting of Au nano-islands and organic layer of terbium(III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate) complex, $Tb(thd)_3$.

2. MATERIALS AND EXPERIMENTAL METHODS

Figure 1 shows the chemical structure of the $Tb(thd)_3$, used in this study as an organic component for fabrication of the planar nanoscale light-emitting device. The $Tb(thd)_3$ was synthesized by the conventional method [9] and used without further purification.

The organic and metal layers were all deposited by thermal evaporation method using a diffusion-pumped vacuum bell-jar system at a pressure of $\sim 3 \cdot 10^{-4}$ Pa. The deposition rate was controlled to 0.1–0.2 nm/s. The thickness of the vacuum deposited (VD) organic films varied from 35 to 120 nm. Complementary measurements were performed on $Tb(thd)_3$ layers deposited by a solution technique (by immersing the Au substrate into a 1 mM solution of native $Tb_2(thd)_6$ in chloroform). Reconstructed Au(111) surfaces for STM measurements

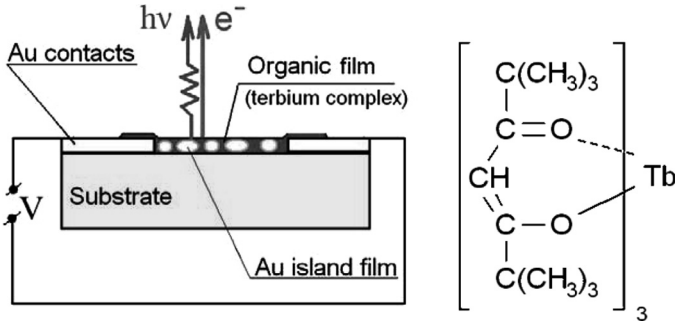

FIGURE 1 A schematic view of the fabricated nanoscale structure and chemical formula of terbium complex, $Tb(thd)_3$.

of $Tb(thd)_3$ monolayers were prepared from polycrystalline gold films ($\sim$150 nm thick) deposited in ultra high vacuum ($\sim 5 \times 10^{-8}$ Pa) onto a freshly cleaved mica surface followed by an annealing in a propane-air flame at 550–600 K. Chemical structure of thin organic layers deposited onto a gold surface either by VD or solution technique was characterized by FTIR and PL spectroscopy. FTIR spectra of the organic layers deposited onto Au surface were measured with Bruker IFS-88 FTIR spectrometer in the spectral range 380–4000 cm^{-1} with spectral resolution of 2 cm^{-1} in a reflection-absorption mode using Harrick-type ATR attachment with IR beam incidence angle of 72°. The number of scans was 256, which was enough to record spectra of high signal-to-noise ratio.

The PL spectra were measured at room temperature by automated SF-4 spectrophotometer (LOMO, St. Petersburg) with 4 nm spectral slit width.

For STM characterization the commercial STM (NT-MDT, Russia) was used. The STM images of deposited $Tb(thd)_3$ layers were recorded in constant current mode at ambient conditions. The STM tips were mechanically cut from a 0.25 mm Pt/Ir (80:20) wire and tested on cleaved highly oriented pyrolitic graphite surfaces. Typical imaging conditions were 0.1–0.5 V in bias voltage and 0.1–1 nA in tunneling current. The error of measured distances was within 5%. Local current-voltage (I–V) characteristics were obtained at a fixed tip-sample distance determined by the imaging voltage and the tunneling current used during image recording. For the recording of local I–V curve, the scan was stopped and the feedback loop was switched off in order to apply a voltage ramp within the limits from -1.2 V to $+1.2$ V. At higher voltages the measurements of I–V curves have not been performed because of influence of electric field on film morphology.

The fabrication procedure of planar nanocomposite device was described in detail elsewhere [6,7]. The organic molecules were deposited onto Au nano-islands grown in a $\sim 30\,\mu$ gap between two gold electrodes. First, gold film contacts were evaporated in UHV onto a glass surface through a mask mounted above the surface forming two electrodes separated with a micro-gap. In a subsequent step, in the case of "dry" deposition of the organic layer, the gold nano-islands were grown into the gap using thermal vacuum evaporation of crystalline Au. In the last step, the organic molecules were deposited in the gap covering the Au nano-islands. When the organic layer was deposited by solution technique ("wet" method), the organic component is deposited first, and after the completion of the molecule deposition, the Au nano-islands were grown in the gap. By passing an electric current through the Au island film, the light emission from the nanocomposite is observed. A schematic view of the nanoscale planar electroluminescent composite device is shown in Figure 1.

3. RESULTS AND DISCUSSION

3.1. Characterization of Deposited Organic Layers by FTIR Spectroscopy and Photoluminescence Analysis

It is clear that the absence of thermal decomposition during the vacuum deposition of the organics is critical for their practical application in OLED devices. However, to our knowledge, only few papers related to the spectroscopic evidence of vacuum deposition behavior of the materials under study were published [10,11]. In the present work, the structure of deposited layers was characterized by FTIR and PL spectroscopy. Figure 2 shows the IR reflection-absorption (RA) spectra of $Tb(thd)_3$ thin VD films on Au surface, and those of $Tb(thd)_3$ self-assembled from chloroform solution on Au surface. FTIR spectra of VD $Tb(thd)_3$ films are identical with those of the films deposited directly from solution and demonstrate several clearly defined bands characteristic of β-diketonate metal complexes [12,13]. These are asymmetric and symmetric C−O stretching bands centered at 1580 and 1403 cm^{-1}, respectively; asymmetric and symmetric C−C stretching bands centered at 1506 and 1356 cm^{-1}, respectively, as well as stretching and bending Tb–O vibration bands centered respectively at 607 and 475 cm^{-1}. However, these spectra are clearly different from the IR spectrum of the initial material prepared as KBr pellet [12]. According to X-ray data, $Ln_2(thd)_6$ complexes convert to $Ln(thd)_3$ when dissolved in organic solvents or heated [14–17]. We observed similar behavior for our terbium complex. The spectra of the films obtained

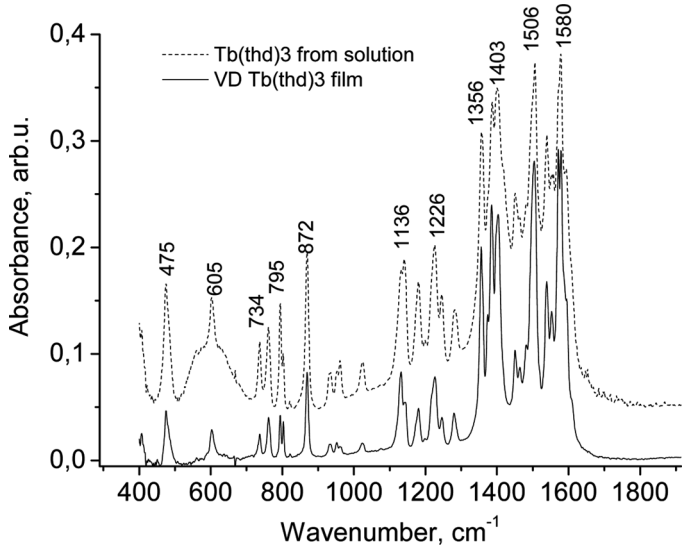

FIGURE 2 FTIR spectra of $Tb(thd)_3$ thin films prepared by vacuum deposition (solid curve) and direct deposition from chloroform solution (dotted curve) on polycrystalline Au surface.

by "wet" technology from chloroform solution and those of the VD films lack the strong absorption band of the C−O< bridging oxygen stretching vibration centered at 1475 cm^{-1}, giving evidence for monomeric structure of terbium complex in the deposited layers. In addition, FTIR spectra of the monomeric terbium complex lack some peaks in the region of C−C stretching and CH bending vibrations between 1300 and 795 cm^{-1}. This suggests that the structure of Ln^{3+} first coordination sphere of $Tb(thd)_3$ in the deposited layers is somewhat different from the structure reported for the crystalline powders.

Satisfactory vacuum deposition behavior of the monomeric material is also confirmed by PL measurements. PL spectra of $Tb(thd)_3$ layers deposited onto Au surface both by "dry" and "wet" technologies (Fig. 3) are identical. However, they differ from the PL spectrum of crystalline $Tb(thd)_3$ reported in the literature [1–3] due to above mentioned subtle changes in the ligand arrangement around Tb^{3+} ions in the films.

3.2. Morphology of Deposited Organic Layers and Local Current-Voltage Characteristics

Morphology of $Tb(thd)_3$ thin film was characterized by STM imaging. The STM image of $Tb(thd)_3$ films evaporated onto polycrystalline Au

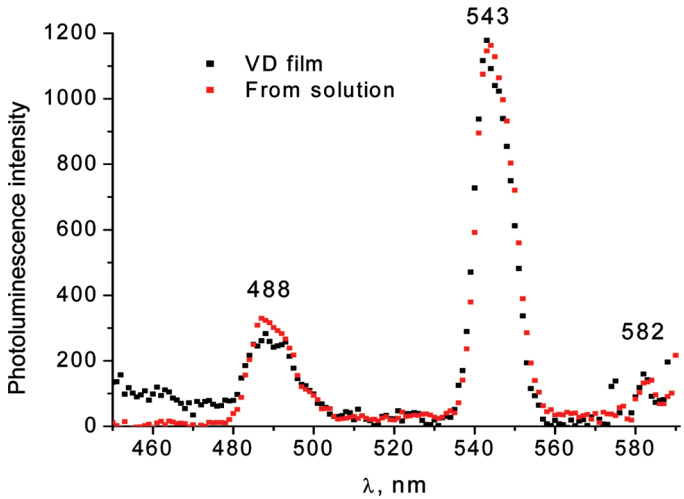

FIGURE 3 Photoluminescence spectra of $Tb(thd)_3$ layers deposited by thermal evaporation in vacuum on polycrystalline Au surface (1) and self-assembled at the Au-liquid interface from chloroform solution.

surface looks almost featureless (Fig. 4a), whereas fairly ordered needle-shaped aggregates appear in the monolayer film deposited from chloroform at liquid-Au(111) interface (Fig. 4c). One can suggest that a possible origin of this difference is a self-assembly of monomeric $Tb(thd)_3$ molecules along the terraces of crystalline Au(111) surface.

The corresponding locally recorded *I–V* curves of the VD $Tb(thd)_3$ films are presented in the right part of Figure 4. For thicker films (Fig. 4a), they are strongly asymmetric with respect to applied voltage being linear at the voltages $-0.8<U<0.5\,V$ and showing the oscillations at higher voltages. The similar behavior, though much more pronounced, was observed for VD layers of $Eu(dbm)_3$bath in our earlier paper [7] and was attributed to loose packing of bulky organic ligands around europium ions and their perturbations induced by the electric field of the STM tip. Smaller oscillating behavior of locally recorded asymmetric *I–V* curves of the VD $Tb(thd)_3$ films indicates that (thd) ligands are more closely packed around terbium ions than the bulkier $(dbm)_3$ bath ligands. The local *I–V* curves measured for nano-sized areas of monolayer $Tb(thd)_3$ films are also linear at the voltages $0 < U < 0.4\,V$ showing a super linear character at voltages above 1 V. The light emission from such films induced by STM tunnel current was observed under the applied voltage of 1.5 V, that corresponds to the local electric field strength of $\sim 3 \cdot 10^8\,V/m$. This value fairly agrees

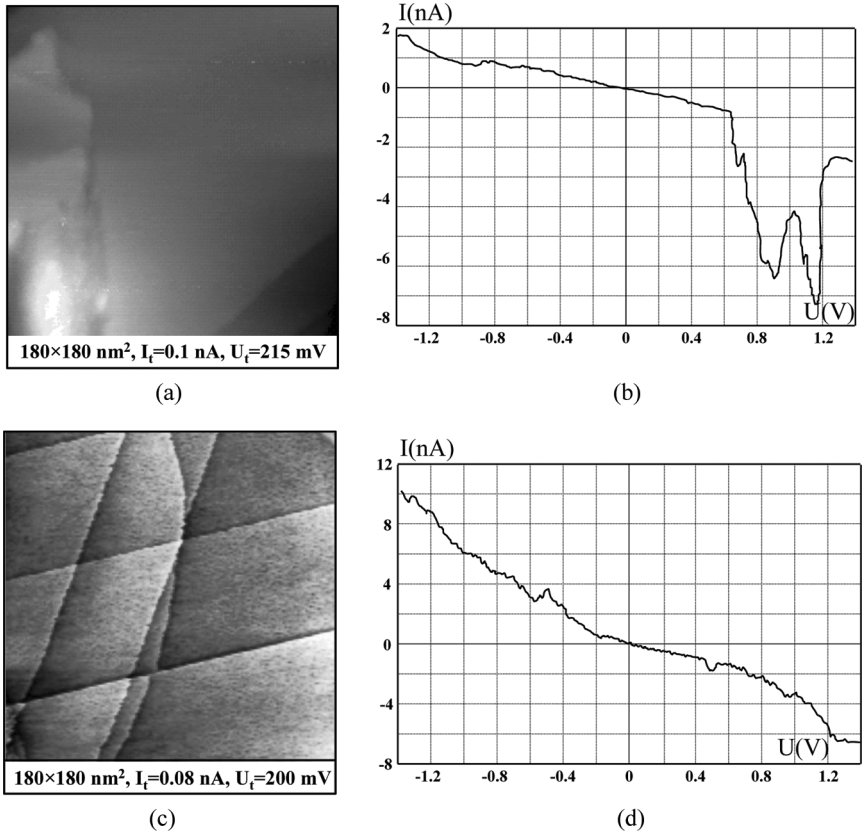

FIGURE 4 STM images and local current-voltage characteristics of $Tb(thd)_3$ layers obtained (a, b) – by vacuum deposition on polycrystalline Au surface; and (c, d) – at liquid-solid interface on reconstructed Au(111) surface.

with the electric field strength value, at which the electroluminescence is usually observed in the metal-organic nanocomposites [7].

3.3. Charge Transport and Electroluminescence Measurements of the Nanocomposite

The measurements of light emission from the fabricated planar nanocomposite were performed on the cell shown in Figure 1. When the applied voltage increases, the current-voltage characteristics measured on these planar nanostructures transform from linear to super linear ones (Fig. 5). The visible light emission from these

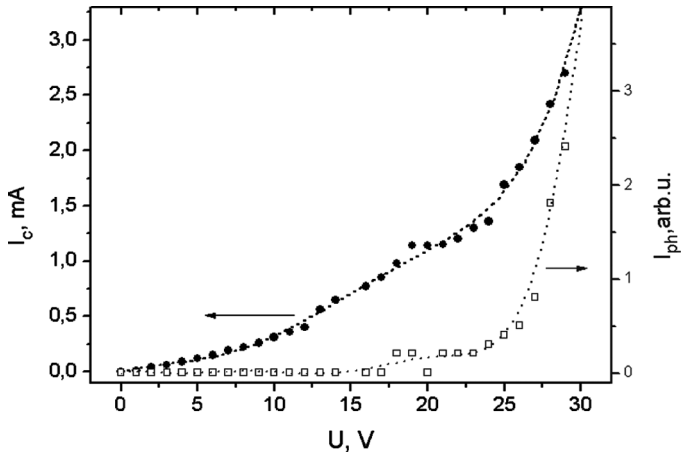

FIGURE 5 Current-voltage characteristic and luminous efficiency versus the applied voltage measured for the nanocomposite consisting of Au nano-islands and $Tb(thd)_3$ layer.

nanostructures was observed at the applied voltage of 10–30 V, and the luminous efficiency of the emission increases when the applied voltage increases (Fig. 5). According to our estimations, the light emission from the nanocomposite occurs at the applied electric field mean strength of $\sim 10^8$ V/cm.

It is known that ensembles of metal nano-particles onto a dielectric substrate emit electrons and photons when these films are energized by passage of current through them or by laser irradiation [8]. The primary recipient of energy is the electron gas, which can be heated up to temperatures much higher than the particle lattice temperature. The major physical factor permitting generation of hot electrons in nano-particles is the dramatic reduction of the electron-lattice energy transfer in the particles whose size is smaller than the mean free path of electrons in the volume. Electrons with energy higher than the work function, are emitted to vacuum. Other electrons can excite the light emission. Its possible mechanism can be bremsstrahlung, inverse surface photoeffect, radiation generated by inelastic tunnelling of electrons between the islands and the radiative decay of plasma excitation.

As it was shown in our previous papers [5,7], the light emission observed under the electric current passage through a nanocomposite structure consisting of island metal films and molecules of rare earth complexes shows the features peculiar to the corresponding organic

compounds and to the metal nano-islands. Therefore, the fabricated planar nanodevice can be used as a light source with controllable emission spectrum both of extended and submicron dimensions.

4. CONCLUSIONS

Planar nanoscale EL structures consisting of Au nano-islands and a terbium complex $Tb(thd)_3$ as the electron-transport emitting layer were fabricated. The $Tb(thd)_3$ layers were characterized by FTIR and PL spectroscopy measurements, which confirm stable vacuum deposition behaviour of $Tb(thd)_3$ or its self-assembly at the Au-liquid interface in the monomeric structure.

Using STM, the morphology of the first near-surface layers of $Tb(thd)_3$ films was investigated, and was found to consist of needle-like structures self-assembled on Au(111) terraces. The ordered structure is lost for the VD films of increased thickness. The locally recorded *I–V* curves of the $Tb(thd)_3$ layers are asymmetric with respect to applied voltage, being linear at the voltages $-0.8 < U < 0.5\,V$, and showing an oscillating behaviour at higher voltages. Super linear character of the *I–V* curves is observed only for self-assembled $Tb(thd)_3$ monolayer on reconstructed Au(111) surface at the voltage $0 < U < 0.4\,V$.

The visible light emission from the fabricated nanoscale structure was observed at the voltages of 10–30 V, showing the luminescence features both of $Tb(thd)_3$ and Au nano-islands. The obtained results can be useful for the design of both the micro-scale and large scale planar metal-organic light-emitting devices with controllable spectral characteristics.

REFERENCES

[1] Kido, J., Nagai, K., & Okamoto, Y. (1993). *J. Alloys and Compounds*, *192*, 30.
[2] Morgado, J., Charas, A., Fernandes, J. A., Gonçalves, I. S., Carlos, L. D., & Alcacer, L. (2006). *J. Physics D: Applied Physics*, *39*, 3582.
[3] Li, Q., Li, T., & Wu, J. (2001). *J. Phys. Chem., B*, *105*, 12293.
[4] Chen, C. H. & Shi, J. (1998). *Coord. Chem. Rev.*, *171*, 161.
[5] Fedorovich, R. D., Gavrilko, T. A., Marchenko, A. A. *et al.* (2003). Electrical conductivity and electroluminescence of planar nanocomposite structures: gold island film-aluminum oxyquinoline In: *Physics, Chemistry and Applications of Nanostructures*, Borisenko, V. E. *et al.* (Eds.), World Scientific: Singapore, 553.
[6] Gavrilko, T., Fedorovich, R., Naumovets, A., Nechytaylo, V., Puchkovska, G., Viduta, L., Marchenko, A., Baran, J., & Ratajczak, H. (2004). *J. Molec. Struct.*, *704*, 163.

[7] Dovbeshko, G., Fesenko, O., Fedorovich, R., Gavrilko, T., Marchenko, A., Puchkovska, G., Viduta, L., Naumovets, A., Vitukhnovskii, A., & Fichou, D. (2006). *J. Molec. Struct.*, *792–793*, 115.
[8] Fedorovich, R. D., Naumovets, A. G., & Tomchuk, P. M. (2000). *Physics Reports*, *328*, 73.
[9] Halls, J. J. M., Walsh, C. A., Greenham, N. C., Marseglla, E. A., Friend, R. H., Morattl, S. C., & Holmes, A. B. (1995). *Nature*, *376*, 498.
[10] Wang, K. Z., Huang, L., Gao, L. H., Jin, L. P., & Huang, C. H. (2002). *Inorg. Chem.*, *47*, 3353.
[11] Wang, K. Z., Li, L. J., Liu, W. M., Xue, Z. Q., Huang, C. H., & Lin, J. H. (1996). *Mater. Res. Bull.*, *31*, 993.
[12] Pinchas, S., Silver, B. L., & Laulicht, I. (1967). *J. Chem. Phys.*, *46*, 1506.
[13] Korsun, V. P. & Kostromina, N. A. (1983). *Ukr. K him. Zhurn.* (Russ. Ed.), *49*, 577.
[14] Mode, V. A. & Smith, G. S. (1969). *J. Inorg. Nucl. Chem.*, *31*, 1857.
[15] Ghotra, J. S., Hart, F. A., Moss, G. P., & Staniforth, M. L. (1973). *Journal of the Chemical Society, Chemical Communications*, *18*, 669.
[16] Erasmus, C. S. & Boeyens, J. C. A. (1970). *Acta Crystallogr. B, 26*, 1843.
[17] Amano, R., Sato, A., & Suzuki, S. (1980). *Chem. Lett.*, *5*, 537.