ROOM TEMPERATURE PHOSPHORESCENCE OF THIANTHRENE DERIVATIVES

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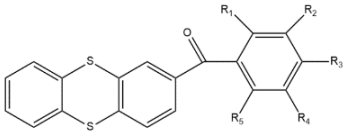
Room-temperature phosphorescence (RTP) has attracted a great deal of attention in the fields of optoelectonric devices [1], high contrast bio-imaging [2], photodynamic therapy [3], photocatalytic reactions [4], and oxygen indicators [5]. Heavy-metal complexes such as iridium complex are commonly used for room temperature phosphorescence but their potential toxicity and instability particularly in case of blue phosphors still remain to be solved. Room temperature phosphorescence from metal-free organic phosphors has attracted much attention in recent years since metal-free phosphors were presented as bright as organometallic compounds, quantum dots, and fluorescent molecules at room temperature [6].

Thianthrene being an electron-donor with a stable mono- and bicationic forms [7,8] has been used in several materials, including small molecules [8,9,10-13]. In particular, phosphorescent properties of thianthrene crystals have already been demonstrated [14], but no study has been performed on its derivatives. Of particular interest are the room temperature phosphorescent (RTP) properties of thianthrene, which suggests this group can be used to promote dual fluorescence-phosphorescence at room temperature in its derivatives.

In this study we present the synthesis of thianthrene derivatives (figure 1) examining the effect of the type of substituent on their RTP properties. The aim of the study is to understand structural and electronic effects, such as produced steric hindrance properties of benzoyl chloride substituents on thianthrene.



Compound	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
R1	H	F	H	H	Br	H	Cl	Cl	Cl	H	F	F	F	H	H
R2	H	H	F	H	H	H	Cl	H	H	Cl	H	H	H	F	F
R3	H	H	H	F	H	Br	H	F	H	F	F	H	H	F	H
R4	H	H	H	H	H	H	H	H	H	H	H	F	H	H	F
R5	H	H	H	H	H	H	H	H	F	H	H	H	F	H	H

Figure 1. Thianthrene molecular structures studied in this work.

[1] D. Chaudhuri, E. Sigmund., A. Meyer et al, MetalFree OLED Triplet Emitters by Side-Stepping Kasha's Rule, *Angew. Chem. Int. Ed*., 52, 13449-13452 (**2013)**

[2] X. Zhen, Y. Tao, Z. An et al, Ultralong Phosphorescence of Water-soluble Organic Nanoparticles for in vivo Afterglow Imaging. *Adv. Mater.*, 29, 1606665 (**2017)**

[3] H.J. Sterenborg, J.W. de Wolf, M. Koning et al, Phosphorescence-fluorescence Ratio Imaging for Monitoring the Oxygen Status During Photodynamic Therapy. *Opt. Express.*, 12, 1873-1878. (**2004)**

[4] a) S. Telitel, F. Dumur, S. Telitel, et al, Photoredox Catalysis Using a New Iridium Complex as an Efficient Toolbox for Radical, Cationic and Controlled Polymerizations under Soft Blue to Green Lights. *Polym. Chem.*, 6, 613-624 (**2015)**; b) M.A. Garcia-Garibay, Advances at the Frontiers of Photochemical Sciences, *J. Am. Chem. Soc.*, 134, 8289-8292 (**2012)**

[5] a) A.S. Mathew, C.A. DeRosa, J.N. Demas et al, Difluoroboron β- diketonate Materials with Long-lived Phosphorescence Enable Lifetime based Oxygen Imaging with a Portable Cost Effective Camera. *Anal. Methods*, 8, 3109-3114 (**2016)**; b) Y. Yu, M.S. Kwon et al, Room-temperature-phosphorescence-based Dissolved Oxygen Detection by Core-shell Polymer Nanoparticles Containing Metal-free Organic Phosphors. *Angew. Chem. Int. Ed*., 56, 162071-16211 (**2017)**

[6] a) R.E. Andrews, K.M. Shah, J.M. Wilkinson et al, Effects of Cobalt and Chromium Ions at Clinically Equivalent Concentrations after Metal-on-metal Hip Replacement on Human Osteoblasts and Osteoclasts: Implications for Skeletal Health. *Bone,* 49**,** 717-723 (**2011)**; b) S.M. Plaza, The Safety and Efficacy of High-dose Chromium. *Altern. Med. Rev.*, 7, 218-235 (**2002)**

[7] L.A. Tinker, A.J. Bard, Electrochemistry in liquid sulfur dioxide. 1. Oxidation of thianthrene, phenothiazine, and 9,10-diphenylanthracene. J Am Chem Soc;101(9):2316-9. (**1979**)

[8] O. Hammerich, V.D. Parker, The reversible oxidation of aromatic cation radicals to dications. Solvents of low nucleophilicity. Electrochim Acta;18: 537- 41. (**1973**)

[9] S. Ogawa, H. Muraoka, R. Sato, Design of reversible organiceorganometallic multi-redox systems using thianthrene having ferrocene fragments. Tetrahedron Lett; 47:2479-83 (**2006**)

[10] J.M. Lovell, R.L. Beddoes, J.A. Joule, Synthesis of 4,6-disubstituted thianthrenes; Xray crystal structures of 4,6-diphenylthianthrene and 1-tetrathiafulvalenylnaphthalene. Tetrahedron; 52(13):4745- 56 (**1996**)

[11] K. Sato, M. Hyodo, M. Aoki et al, Oxidation of sulfides to sulfoxides and sulfones with 30% hydrogen peroxide under organic solventand halogen-free conditions. Tetrahedron; 57:2469-76 (**2001**)

[12] K. Sun, W. Jiang, X Ban et al, Novel aggregationinduced emission and thermally activated delayed fluorescence materials based on thianthrene-9,9',10,10'-tetraoxide derivatives. RSC Adv; 6: 22137- 43 (**2016**)

[13] M. Wroblowska, A. Kudelko, N. Kuznik et al, Synthesis of extended 1,3,4-oxadiazole and 1,3,4-thiadiazole derivatives in the Suzuki cross-coupling reactions. J Heterocycl Chem (**2016**)

[14] A. Arena, S. Campagna, A.M. Mezzasalma et al, Analysis of the phosphorescence of thianthren crystals. Il Nuovo Cimento;15(12): 1521-32 (**1993**)