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Synthesis and Spectroscopic Properties of Propeller Typed 2,4,6-Tri(anthracen-9-yl)-1,3,5-triazine

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The novel propeller typed compound, 2,4,6-tri(anthracen-9-yl)-1,3,5-triazine (**TAT**) with C_3 symmetry was synthesized by using 9-anthryl lithium with 1,3,5-trichlorotriazine or 2-chloro-4,6-dimethoxy-1,3,5-triazine in the presence of palladium catalyst in 22-48% yield. Another two propeller-liked compounds, 2-(anthracen-9-yl)-4,6-dimethoxy-1,3,5-triazine (**3**) and 2,4-di(anthracen-9-yl)-6-methoxy-1,3,5-triazine (**4**) were obtained at same time. The propeller typed structures of **TAT**, **3** and **4** were confirmed by crystal analysis and theoretical calculations. The intramolecular C-C bond rotations between the anthryl groups and the triazine units in molecule **TAT**, **3** and **4** were regarded as the key factor to understand their spectroscopic behaviors in fluid mediate and rigid solution.

Introduction

As a versatile and readily available molecule, 1,3,5-triazine is well-known in organic chemistry. Such C_3-symmetric molecule has been widely used for molecular construction in supramolecular chemistry[1], coordination chemistry[2] and drug synthesis.[3] Recently, the π-conjugated 1,3,5-triazine derivatives including small molecules, dendrimers[4] and polymers[5] have exhibited good optical and electrical properties and showed applications in organic light emitting diodes (OLED).[6]

Among 1,3,5-triazine-based derivatives, triaryl triazine compounds are very attractive to organic chemists due to their C_3-symmetric molecular structures. There are several methods including Friedel–Crafts reaction[7], Suzuki-coupling[8] and trimeric cyclization[2b,5a,9] of aromatic nitriles for the preparation of triaryl triazine compounds. 2,4-6-Triphenyl-1,3,5-triazine (**TPT**, Fig. 1)[10] has received many reports including both syntheses and opt-electrical properties. In our previous work, 2,4-6-trinaphthan-1-yl-1,3,5-triazine (**1-TNT**) and 2,4-6-trinaphthan-2-yl-1,3,5-triazine (**2-TNT**) were synthesized via Suzuki reaction and their spectroscopic behaviors were studied in both solution and LB films[11].

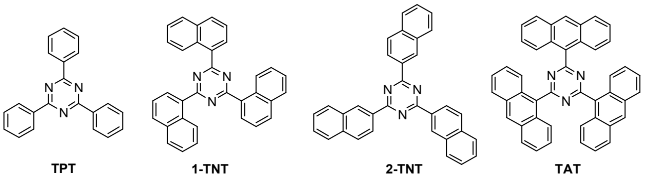
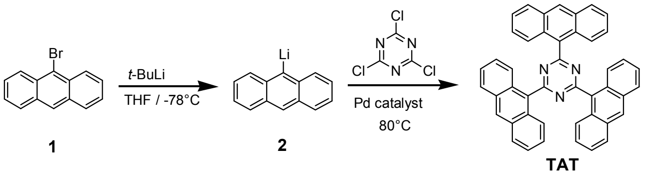


Fig. 1 The molecular structures of 2,4-6-triaryl-1,3,5-triazines

In this paper, we try to report the synthesis of a novel compound, 2,4,6-tri(anthracen-9-yl)-1,3,5-triazine (**TAT**, Fig. 1) with a structure of "propeller" in C_3 symmetry, starting from 9-anthryl lithium and 1,3,5-trichlorotriazine or 2-chloro-4,6-dimethoxy-1,3,5-triazine in the presence of palladium catalyst. It is interesting to find that the rotation of C-C bond between anthryl ring and triazine ring is the key to understand the spectroscopic behaviors of **TAT**. In addition, the side-products, **3** and **4** bearing one and two anthryl groups, respectively are also studied in both synthesis and photophysical behaviors.

Results and discussion

Scheme 1 shows the synthetic route to **TAT**. There are two steps in making **TAT**. The first one is Br/Li exchange between 9-bromoanthracene and *t*-BuLi in dry THF at –78 °C. The second step is the coupling reaction of the obtained 9-anthryl lithium (**2**) with 1,3,5-trichlorotriazine in the presence of palladium catalysts. In our case, aryl lithium (**2**) is employed, so the coupling step is a Kumada coupling-like reaction[12]. We have found that the coupling reaction can not be occurred without catalyst. We have also found that $NiCl_2(dppf)_2$ did not work as catalyst for this reaction. Palladium catalysts, including $PdCl_2(dppf)_2$, $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$ and $Pd(OAc)_2$ are employed for the reaction (see Table 1). When $PdCl_2(dppf)_2$ is used as catalyst, the coupling reaction can occur smoothly at 80 °C with 48% yield of **TAT**.



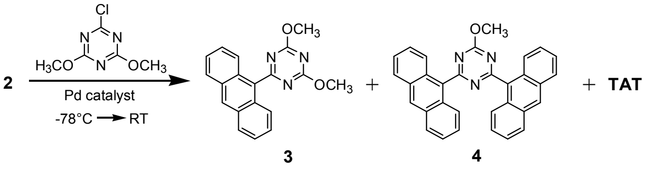
Scheme 1. The first synthetic route to **TAT**

Table 1. The formation of **TAT** using 1,3,5-trichloro-triazine

Entry	Pd catalyst (0.03 eq)	**TAT** (%)
1	$PdCl_2(dppf)_2$	48
2	$Pd(PPh_3)_4$	42
3	$Pd(PPh_3)_2Cl_2$	37
4	$Pd(OAc)_2$	22

In order to study on the spectroscopic behaviors of **TAT**, a model compound, 2-(anthracen-9-yl)-4,6-dimethoxy-1,3,5-triazine (**3**) is necessary to be prepared. Firstly, we designed to synthesize **3** with **2** and 2-chloro-4,6-dimethoxy-1,3,5-triazine in presence of $PdCl_2(dppf)_2$ (Scheme 2). When 1 equiv of **2** was employed, **3** was obtained in 33% yield. Unexpected side products, **4** and **TAT** were given in 28% yield and 6%, respectively at same time (Entry 1, Tabel 2). If 3 equiv of **2** was employed, only **TAT** was obtained in 40% yield (Entry 3, Tabel 2). If 2 equiv of **2** was employed, the main products were **TAT** and **4** in 11% and 28% yields, respectively. Only trace amount of **3** could be observed in this case (Entry 2, Tabel 2). Other palladium catalysts, including $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$ and $Pd(OAc)_2$ were also employed for this coupling reaction (see Table 2). On the whole, all four Pd catalysts show similar catalysis behaviors. However, $PdCl_2(dppf)_2$ shows better selectivity, and $Pd(OAc)_2$ seems weaker catalytic efficiency.

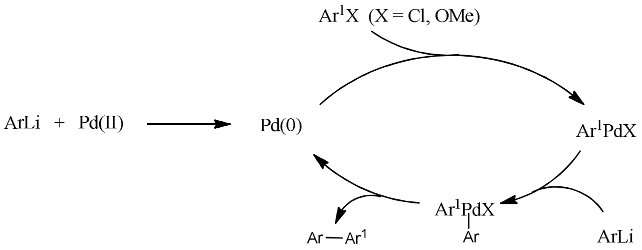
From above synthetic work, we have developed two efficient synthetic routes in making **TAT** in moderate yields. However, the second route (Scheme 2) shows more interests in generation of side products, **3** and **4**.



Scheme 2 The second synthetic route to **TAT**

Table 2 The formation of **TAT**, **3** and **4** using 2-chloro-4,6-dimethoxy-1,3,5-triazine (Pd catalyst: 0.01 eq)

Entry	Pd catalyst	**2** (eq)	**TAT** (%)	**3** (%)	**4** (%)
1	$PdCl_2(dppf)_2$	1.0	6	33	28
2	$PdCl_2(dppf)_2$	2.0	11	trace	28
3	$PdCl_2(dppf)_2$	3.0	40	--	--
4	$Pd(PPh_3)_4$	1.0	16	37	35
5	$Pd(PPh_3)_4$	2.0	15	12	29
6	$Pd(PPh_3)_4$	3.0	39	6	25
7	$Pd(PPh_3)_2Cl_2$	1.0	12	36	32
8	$Pd(PPh_3)_2Cl_2$	2.0	11	12	35
9	$Pd(PPh_3)_2Cl_2$	3.0	36	20	6
10	$Pd(OAc)_2$	1.0	5	33	2
11	$Pd(OAc)_2$	2.0	10	16	22
12	$Pd(OAc)_2$	3.0	25	13	5



Scheme 3. The possible mechanism for formation of Ar-Ar^1

We speculate that the reaction follow a Pd-catalyzed Kumada-type mechanism[12] (Scheme 3), wherein oxidative addition of aryl halides to Pd(0) is faster than aryl-OMe. The latter features a much stronger bond strength which is normally inert to Pd(0). In our case, the highly electron-deficient triazine ring should significantly activate the C-O bond, and therefore promote the corresponding oxidative addition step. Consequently, production of **3** should be the most facile step.

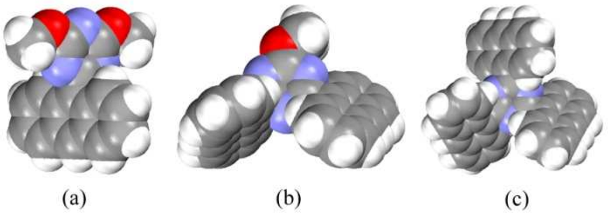


Fig. 2 The molecular configurations of **3** (a), **4** (b) and **TAT** (c). The top view of the **3** (a) and **4** (b) in their single crystals; The top view (c) of **TAT** optimized by theoretical calculations at B3LYP/6-31G(d) level.

We have also obtained the crystal structures of **3** and **4**, which are shown in Fig. 2-a and Fig. 2-b. The crystal **3** belongs to triclinic space group P-1. The two methoxyl groups are planar to the centre triazine ring. The torsion angles of C16-N3-O1-C18 and C15-N2-O2-C19 are 0.09° and 0.43°, respectively. The interplanar angle between the anthryl ring and triazine ring is observed as 68.67°. The crystal **4** belongs to monoclinic space group P2(1)/n. Similar to the case of **3**, the methoxyl group is also planar to the triazine ring in **4**. The torsion angle of N1-C16-O1-C18 is 1.11°. The interplanar angles between the anthryl rings and triazine ring are observed as 89.77° and 54.43°, respectively. The interplanar angle between the two anthryl rings is observed as 66.26°. Unfortunately, we have not obtained the crystal of **TAT**, but its theoretical calculations were undertaken at B3LYP/6-31G(d) level. Calculations have provided some insight into the structural differences among the structures of **3**, **4** and **TAT** (Fig. 2-c). In molecule **TAT**, the average interplanar angle between the anthryl ring and triazine ring is measured as 55.32°. The average interplanar angle between neighbouring two anthryl rings is measured as 89.17°. Compared with the structures of **3** and **4**, molecule **TAT** clearly shows the "Propeller" typed framework with C_3 symmetry.

UV-vis absorption spectrum of **TAT** shows absorption band with fine structure at long wavelength, and the maximum peak is at 387 nm (ε = 1.25×10^{4} $M^{-1}\cdot cm^{-1}$, Fig. 3) in THF. At meanwhile, **3** and **4** show their maximum peaks at 383 nm (ε = 6.11×10^{3} $M^{-1}\cdot cm^{-1}$) and 385 nm (ε = 8.62×10^{3} $M^{-1}\cdot cm^{-1}$), respectively. Compound **3**, **4** and **TAT** have similar absorption behaviors due to their similar molecular structures with same anthryl chromophore. Their molar extinction coefficient difference is due to their different quantities of anthryl groups. The symmetric molecular structures imply that **3**, **4** and **TAT** show weak polarities, which make small difference in their absorption behaviors in different polarity of organic solvents (Table 3).

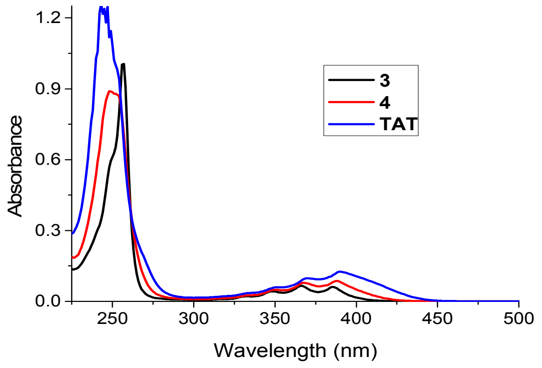


Fig. 3 UV-vis spectra of **3**, **4** and **TAT** in THF ([C] = 1E-5 M)

Table 3. Date of UV-vis spectra and fluorescence spectra of **3**, **4** and **TAT** in organic solvents.

	Compd	*n*-hexane	chloroform	tetrahydrofuran	ethyl acetate	acetonitrile
λ_{max}^{abs} (nm)	**TAT**	385	388	387	386	386
λ_{max}^{em} (nm)	**TAT**	495	504	509	511	513
Φ_f	**TAT**	0.58	0.30	0.18	0.13	0.06
λ_{max}^{abs} (nm)	**3**	380	384	383	382	382
λ_{max}^{em} (nm)	**3**	489	502	503	511	515
Φ_f	**3**	0.58	0.31	0.23	0.15	0.08
λ_{max}^{abs} (nm)	**4**	383	386	385	384	384
λ_{max}^{em} (nm)	**4**	491	503	506	506	510
Φ_f	**4**	0.46	0.26	0.20	0.17	0.01

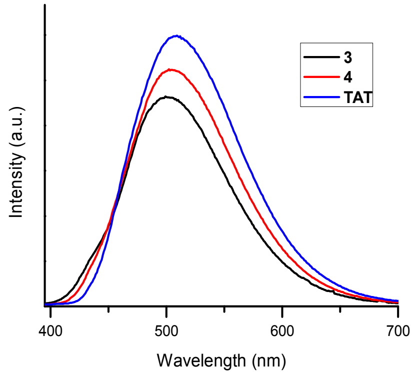


Fig. 4 Fluorescene spectra of **3**, **4** and **TAT** in THF ([C] = 1E-5 M, λ_{ex} = 385 nm, slit: 4/4)

In the excited state, **3**, **4** and **TAT** show similar flourescence emission as single peaks at 503, 506 and 509 nm, respectively without fine structure in THF (Fig. 4) , which is ascribed to the intramolecular charge transfer (ICT) state emission[13,14]. Their lifetimes were measured in THF solution ([C] = 1E-5 M) as 3.51, 2.92 and 2.70 ns for **3**, **4** and **TAT**, respectively. The co-planarity between anthryl and triazine moieties can be formed by rotation of C-C bond. In this case, the π-electron clouds of two moieties are overlap and the process of ICT between anthryl and triazine moieties can be occurred in the excited state. From the data in Table 3, we can clearly find that the ICT emission peaks show slightly bathochromic shift when the polarity of solvent increased. Normally, ICT emission is heavily dependent on the polarity of solvent. Large polar solvent may stabilize the excited polar D-A molecule by solvation. ICT emission shows large bathochromic shift when the polarity of solvent increased. The slightly bathochromic shift behaviors of ICT emission for **3**, **4** and **TAT** can be attributable to their symmetric molecular structures, which make small changes of the dipole moments of molecules in excited state compared with that in ground state.

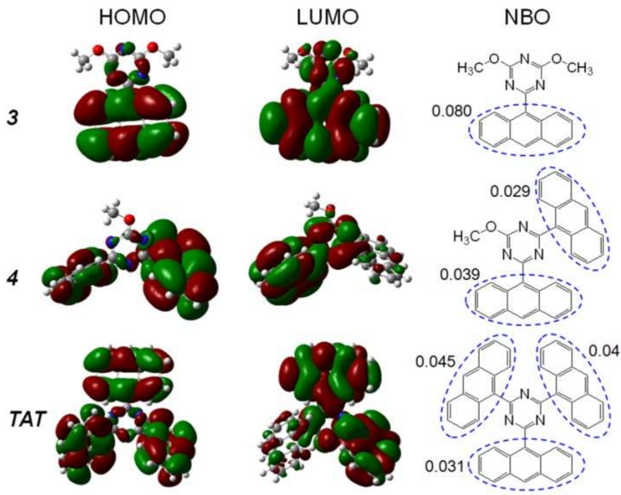


Fig. 5 The highest occupied molecular orbitals (HOMO), the lowest unoccupied molecular orbitals (LUMO) and natural of bond orbitals charges (NBO) of **3**, **4** and **TAT**.

ICT flourescence is an emission from excited state of conjugated D-A compound. In our case, anthracene moiety is the electron donor (D) and the triazine moiety is the electron acceptor (A). The HOMO (highest occupied molecular orbits), LUMO (lowest unoccupied molecular orbits) and NBO (natural of bond orbitals) charges of **3**, **4** and **TAT**, which are optimized by theoretical calculations at B3LYP/6-31G(d) level are shown in Fig. 5. We can see clearly that the electron cloud distribution on 1,3,5-triazin unit increase from HOMO to LUMO for all three compounds. The NBO charges are all positive for the anthryl units in these compounds, which illustrate the intramolecular charge transfer between anthryl and 1,3,5-triazine units.

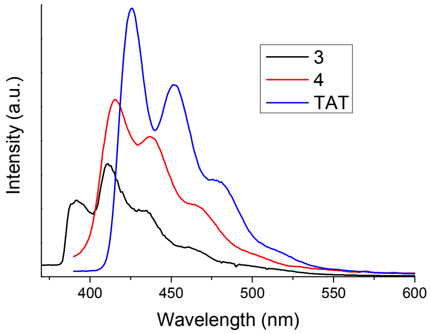


Fig. 6 Fluorescene spectra of **TAT**, **3** and **4** in 2-MTHF at 77K ([C] = 1E-5 M, λ_{ex} = 360 nm for **3**, λ_{ex} = 380 nm for **4** and **TAT**, slit: 2/2).

However, no ICT state emission could be observed at 77 K in a glass solution of 2-methyl tetrahydrofuran (2-MTHF), only anthracene-like emission with fine structure was found for **3**, **4** and **TAT** (Fig. 6). In the rigid solution, the anthryl group and the triazine moiety are frozen, no ICT state emission observed implies that the intramolecular C-C bond rotations between anthryl and triazine moietis are frozen, and non-conjugation could be formed between the two moieties. The reason is due to the big interplanar angles between the anthryl ring and triazine ring, which can clearly be observed from their crystal structures (Fig. 2). For example, in molecule **3**, the interplanar angle between the anthryl ring and triazine ring is observed as 68.67° (Fig. 2), which could be kept in both ground state and excited state in rigid solution (77 K). Two moieties are not conjugated in this case, only anthryl group (chromophore) itself gives anthryl-like fluorescene emission for **3**, **4** and **TAT**.

With the increase of anthryl groups, the emission shows bathochromic shift from **3**, **4** to **TAT** (Fig. 6). Compound **3**, **4** and **TAT** are D-A compounds, although no conjugation in rigid solution (77 K), the intramolecular electron induced effect should exist in these D-A compounds. We can found that the NBO charges are all positive for the anthryl units in these compounds (Fig. 5), which partially means the existence of intramolecular electron induced effect. Therefore, with the increase of anthryl groups, stronger intramolecular electron induced effect occurred to **TAT** than that to both **4** and **3**. **TAT** shows lower energy gap in the excited state, which gives longer wavelength emission (bathochromic shift) compared with that of **3** and **4**.

Conclusions

In conclusion, we have efficiently synthesized the novel propeller typed compound, **TAT** by using 9-bromoanthracene and 1,3,5-trichlorotriazine or 2-chloro-4,6-dimethoxy-1,3,5-triazine as raw materials in the presence of palladium catalysts. Another two propeller typed compounds **3** and **4** were also obtained as side products. Their propeller typed structures are confirmed by crystal analysis and theoretical calculations. The intramolecular C-C bond rotation between anthryl group and triazine moiety in these three compounds is the key factor to understand their spectroscopic behaviors difference in fluid mediate and rigid solution. Our work gives a good example to comprehend the photophysical behaviors from these novel propeller-typed molecular structures. In addition, such functionalized compounds, **3**, **4** and **TAT** might be applied in organic functional materials,[6] such as EL, NLO etc.

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Notes and references

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† Electronic supplementary information (ESI) available: General experimental procedures, spectroscopic data (^{1}H-NMR, ^{13}C-NMR and HRMS), crystal data in CIF and theoretical calculations for the corresponding products. CCDC 1045919 for **3** and CCDC 1045920 for **4**. See DOI: 10.1039/b000000x/

1 (a). S. Li, S.-X. Fa, Q.-Q. Wang, and M.-X. Wang, *J. Org. Chem.* 2012, **77**, 1860; (b) D.-X. Wang, Q.-Y. Zheng, Q.-Q. Wang and M.-X. Wang, *Angew. Chem. Int. Ed.* 2008, **47**, 7485. (c) P. G. A. Janssen, J. Vandenbergh, J. L. J. van Dongen, E. W. Meijer and A. P. H. J. Schenning, *J. Am. Chem. Soc.* 2007, **129**, 6078. (d) T. Kusukawa and M. Fujita, *J. Am. Chem. Soc.* 2002, **124**, 13576.

2 (a) S. Anke, S. Tatyana and K. Edwin, *Coord. chem. Rev.* 2013, **257**, 2032. (b) B. Therrien, *J. Organomet. Chem.* 2011, **696**, 637.

3 (a) A. Kumar and S. K. Menon, *Eur. J. Med. Chem.* 2009, **44**, 2178. (b) G. Blotny, *Tetrahedron* 2006, **62**, 9507. (c) C. B. Vu, D. Pan, B. Peng, G. Kumaravel, G. Smits, X. Jin, D. Phadke, T. Engber, C. Huang, J. Reilly, S. Tam, D. Grant, G. Hetu and R. Petter, C. *J. Med. Chem.* 2005, **48**, 2009.

4 (a) E. E. Simanek, H. Abdou, S. Lalwani, J. Lim, M. Mintzer, V. J. Venditto and B. Vittur, *Proc. R. Soc. A* 2010, **466**, 1445. (b) A. P. Umali, H. L. Crampton and E. E. Simanek, *J. Org. Chem.* 2007, **72**, 9866. (c) M. B. Steffensen and E. E. Simanek, *Org. Lett.* 2003, **5**, 2359.

5 (a) Y. Xu, S. Jin, H. Xu, A. Nagai and D. Jiang, *Chem. Soc. Rev.* 2013, **42**, 8012. (b) G. Giacomelli, A. Porcheddu and L. de Luca, *Curr. Org. Chem.* 2004, **8**, 1497.

6 (a) A. M. Prokhorov and D. N. Kozhevnikov, *Chem. Heterocycl. Comp.* 2012, **48**, 1153. (b) J. Liu, M.-Y. Teng, X.-P. Zhang, K. Wang, C.-H. Li, Y.-X. Zheng and X.-Z. You, *Org. Elect.* 2012, **13**, 2177. (c) S.-J. Ren, D.-L. Zeng, H.-L. Zhong, Y.-C. Wang, S.-X. Qian and Q. Fang, *J. Phys. Chem. B* 2010, **114**, 10374. (d) H.-F. Chen, S.-J. Yang, Z.-H. Tsai, W.-Y. Hung, T.-C. Wang and K.-T. Wong, *J. Mater. Chem.* 2009, **19**, 8112. (e) R. A. Klenkler, H. Aziz, A. Tran, Z. D. Popovic and G. Xu, *Org. Elect.*

2008, **9**, 285. (f) H.-L. Zhong, E.-J. Xu, D.-L. Zeng, J.-P. Du, J. Sun, S.-J. Ren, B. Jiang and Q. Fang, *Org. Lett.* 2008, **10**, 709.

7 G. Gonn and S. Eisler, *Org. Lett.* 2011, **13**, 5080.

8 (a) L. Xu, W. Wu and H. Wang, *Imaging Science and Photochemistry* (Chinese), 2013, **31**, 375. (b) L. Zou, Y. Liu, N. Ma, E. Macoas, J. M. G. Martinho, M. Pettersson, X. Chen and J. Qin, *Phys. Chem. Chem. Phys.* 2011, **13**, 8838. (c) H. Lee, D. Kim, H.-K. Lee, W. Qiu, N.-K. Oh, W.-C. Zin and K. Kim, *Tetrahedron Lett.* 2004, **45**, 1019. (d) D. Janietz and M. Bauer, *Synthesis* 1993, 33.

9 (a) S.-J. Su, C.-H. Cai, J. Tankmatsu and J. Kido, *Org. Electron.* 2012, **13**, 1937. (b) S. W. Yuan, B. Dorney, D. White, S. Kirklin, P. Zapol, L. P. Yu and D. J. Liu, *Chem. Commun.* 2010, **46**, 4547. (c) H.-F. Chen, S.-J. Yang, Z.-H. Tsai, W.-Y. Hung, T.-C. Wang and K.-T. Wong, *J. Mater. Chem*. 2009, **19**, 8112.

10 (a) A. L. Isfahani, I. Mohammadpoor-Baltork, V. Mirkhani, A. R. Khosropour, M. Moghadam, S. Tangestaninejad and R. Kia, *Adv. Syn. Catal.* 2013, **355**, 957. (b) S. Biswas and S. Batra, *Euro. J. Org. Chem.* 2012, **18**, 3492. (c) D. Cui, M. Nishiura and Z. Hou, *Angew. Chem., Int. Ed.* 2005, **44**, 959. (d) X. Chen, S.-D. Bai, L. Wang and D.-S. Liu, *Heterocycles* 2005, **65**, 1425.

11 Y.-Q. Cai,; W. Wu, H. Wang, J. Miyake and D.-J. Qian, *Surf. Sci.* 2011, **605**, 321.

12 C. Wolf and H. Xu, *J. Org. Chem.*, 2008, **73**, 162.

13 L.-O. Pålsson, C. Wang, A. S. Batsanov, S. M. King, A. Beeby, A. P. Monkman and M. R. Bryce, *Chem.- A Euro. J.* 2010, **16**, 1470.

14 (a) Z.-Y. Li, C.-L. Li, C.-M. Zhao, W. Wu and H. Wang, *J. Lumin.*, 2012, **132**, 2794. (b) C.-L. Li, Z.-Y. Li, L. Xu, H. Han and H. Wang, *Imaging Science and Photochemistry* (Chinese), 2011, **29**, 24.