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Solid-state white-light emission from a pyrylium dye obtained in one synthetic step

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Seven pyrylium salts have been synthesized by condensation of *p*-substituted acetophenones and acetic anhydride, and characterized their photophysical features. One of the prepared compounds (7) constitutes the first example of pyrylium dye displaying white light emission in the solid state.

During the last decades, a great effort has been devoted to the development of new organic materials with appropriate emissive properties in the solid state. Materials for the manufacture of optoelectronic devices such as light-emitting diodes (OLEDs) and organic light-emitting field-effect transistors (OLEFETs) are under a permanent innovation process. The search for systems with higher emission quantum yields (Φ_F) along with simpler production processes is a constant objective for the technological industry. However, most fluorescent molecules in solution become non-emissive in the condensed phase due to processes inhibiting the radiative decay from the excited to the ground state (aggregation- caused quenching, ACQ), typically due to intermolecular interactions, although not limited to this reason.[1]
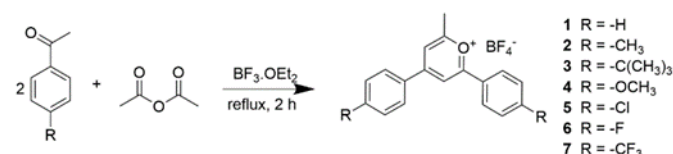
Molecules able to avoid the quenching process in the solid phase comprise, for instance, unsymmetrical triarylamines,[2] dipiperidinobenzenes,[3] tetraphenylethylenes,[4] siloles,[5] benzoxazole and benzothiazole derivatives,[6] biindenyls[7] and tetrasubstituted benzenes.[8] Interestingly, some of these molecules have been implemented in practical devices shortly after the basic development. For instance, Ishow's triarylamines were converted into solid-state lasers[9] whereas Zhang's tetrasubstituted benzenes have been used recently to create optical waveguides.[10]

Within the field of solid-state emitters, there is a growing interest for finding systems capable of attaining a much complex objective like emitting white light. To reach this goal, two strategies have been followed. On the one hand to combine two fluorophores, in a host matrix, one emitting in the blue region of the spectrum and the other in the orange-red part, in such a way that the combination of them yields the desired white luminescence. This is the case, for instance, of naphthalimide and triazine derivatives contained in silica nanoparticles,[11] or of hexanuclear molybdenum clusters embedded in an ureasil matrix.[12] On the other hand, another strategy is the synthesis of organic molecules displaying broad emission bands in the range 400-700 nm. This latter approach is very attractive from the practical point of view, and has led recently to interesting molecules that afford white-light emission like, for instance, difunctional 4-pyridone,[13] substituted benzophenones,[14] triazole derivatives,[15] oxazole compounds,[16] *o*-carborane derivatives,[17] 4-chlorobenzoyldibenzothiophene[18] and 1,2,3,4-tetraphenyloxazolium cations.[19]

Several reviews have covered the field of solid-state emissive materials, including white-light emitters, all showing examples of rational and combinatorial approaches for the discovery of emissive molecular, macromolecular and soft materials.[1,20] Currently there is a consensus in the need for simple operational procedures for the synthesis of the luminescent materials. As stated by M. Shimizu et al. in 2010: 'High quantum yield is only one of the requirements for versatile emitting materials. Simple, cheap, efficient preparations, effortless purification, are all essential for practical applications'.[20a]

In this regard we would like to report the synthesis of seven pyrylium salts (**1**-**7**, see **Scheme 1**) and their emissive properties, both in solution and in the solid state. Among those dyes, compound **7** stands out because its luminescence in powder (when evaporated from acetonitrile) meet the criteria of the *Commission Internationale de l'Eclairage* (CIE) for white-light emission.

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Electronic Supplementary Information (ESI) available: synthesis and characterization of compounds **1**-**7**, spectral details and DFT calculations. See DOI: 10.1039/x0xx00000x

Scheme 1. Synthetic process for compounds **1**-**7**.

1 R = -H
2 R = -CH$_3$
3 R = -C(CH$_3$)$_3$
4 R = -OCH$_3$
5 R = -Cl
6 R = -F
7 R = -CF$_3$

This result is notable from the practical point of view since, although the emission Φ_F is moderate (9%), this salt is made in one-step from commercially available starting materials, and its purification is done just by precipitation. The results here presented can be an opportunity to expand the family of known dyes showing white-light emission to the group of pyrylium compounds. These salts have been studied so far in fields as diverse as photocatalysis,[21] photodynamic therapy,[22] fluorescent cellular probes,[23] chemosensors,[24] polarity probes,[25] nanoparticle characterization[26] and Raman probes.[27] Scarce studies have been published describing the emission of solid samples of pyrylium salts, most of them from the qualitative viewpoint.[28] To the best of our knowledge, there is no precedent of describing a pyrylium dye as a white-light emitter. Only a related cation (based on the 4'-methoxyflavylium structure) has been described recently by I. E. Serdiuk as white-light fluorophore.[28d]

Synthesis of **1-7** was accomplished by means of a condensation reaction between acetic anhydride and two molecules of the corresponding *p*-substituted acetophenone in the presence of BF$_3$-etherate as catalyst (**Scheme 1**).[29] After 2 h of reaction at 138 ºC, the colored solution was poured into excess of diethyl ether and the precipitated product was recovered by simple filtration. After washing with abundant ether, multigram samples of the dyes can be obtained (20 - 35 % yields) with excellent purity (checked by ^{1}H / ^{13}C NMR and high-resolution mass spectrometry, HR-MS). Full characterization details can be seen in the **Electronic Supporting Information (ESI)**. The thermal properties have been measured (DSC, TGA; see Table S1), and it has been found that **1-7** are stable below 240°C (in the same range of temperatures than those reported for other pyrylium salts[28e]).

In dichloromethane (DCM) and acetonitrile (ACN) solutions, pyrylium dyes display bluish fluorescence except for **4**, with electron-donating methoxy groups, which has the emission displaced to longer wavelengths (**Figure 1a**). This band is affected by the polarity of the solvent suggesting the charge-transfer nature of the first singlet excited state (S$_1$), i.e. occurring the transfer from the external electron-rich aromatic rings to the central electron-poor pyrylium core, in accordance with the observations made for other pyrylium derivatives.[30] Additionally, the shift of the absorption bands towards higher wavelengths in DCM, as compared to ACN, is also compatible with this explanation and matches the behavior of related pyrylium dyes.[30]

All the studied compounds are strongly emissive, with fluorescence Φ_F ranging from 0.25 to 0.82 (see **Table 1** for all the collected data) and with emission lifetimes (τ) ranging from 1.0 to 3.7 ns. Calculated radiative constants using both Φ_F and τ ($k_r = \Phi_F$ / τ) afford two subsets of values: k_r ^{DCM} in the range 2.5-2.8 x 10^8 s^{-1} and k_r ^{ACN} in the range 1.5-1.9 x 10^8 s^{-1}. Hucke et al. found that the k_r ^{ACN} of triarylpyrylium dyes is about 10-30% lower than the corresponding k_r ^{DCM}, which is corroborated in the present study.[30]

Table 1. Photophysical parameters in solution for compounds **1-7**.

|	Solv.	λ_{abs} (log ε) (nm)	λ_{em} (nm)	Φ_F	τ (ns)	k_r/10^8 (s^{-1})
1	DCM	345 (4.36), 383 (4.50)	436	0.38	1.5	2.5
	ACN	333 (4.22), 368 (4.27)	440	0.51	3.4	1.5
2	DCM	360 (4.40), 407 (4.62)	453	0.50	2.0	2.5
	ACN	349 (4.31), 388 (4.45)	465	0.63	3.7	1.7
3	DCM	363 (4.48), 410 (4.72)	453	0.54	2.0	2.8
	ACN	350 (4.26), 390 (4.37)	461	0.62	3.3	1.9
4	DCM	384 (4.42), 448 (4.76)	499	0.82	3.2	2.5
	ACN	371 (4.34), 425 (4.60)	516	0.35	2.3	1.5
5	DCM	362 (4.21), 400 (4.38)	455	0.39	1.5	2.5
	ACN	346 (4.35), 378 (4.45)	477	0.51	3.3	1.5
6	DCM	349 (4.40), 388 (4.54)	437	0.46	1.8	2.5
	ACN	338 (4.28), 371 (4.36)	447	0.60	3.7	1.6
7	DCM	334 (4.40), 362 (4.42)	416	0.25	1.0	2.5
	ACN	321 (4.26), 352 (4.25)	420	0.36	2.3	1.6
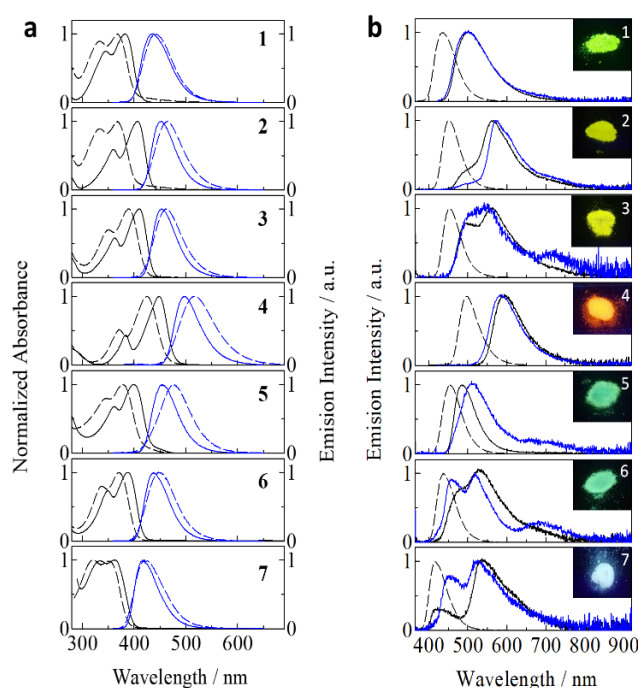
Figure 1. (a) Absorption (black) and fluorescence (blue) spectra of compounds **1-7** in DCM (full) and ACN (broken). The excitation wavelength for the emission spectra was set at 340 nm (360 nm for compound **4**); (b) Fluorescence spectra for compounds **1-7** obtained in DCM solution (broken) and in the solid state evaporated from DCM (black) and ACN (blue). Inset: emission features in the solid state (evaporation from ACN) under UV illumination (365 nm).

It has been reported that the conditions for the preparation of the solids, either crystalline or amorphous, can have a powerful influence on the emission of the molecules, due to the different polymorphs that can be formed.[31] Taking this possibility into account, two solutions of each pyrylium salt were prepared, one in DCM and another in ACN, and then allowed to evaporate, leading to powders whose spectral features, including solid-state Φ_F, were determined using an integrating sphere (**Table 2**). As it can be seen in **Figure 1b**, the emission wavelengths of all the studied compounds are shifted to lower energies, as compared to the fluorescence spectra in solution. This

phenomenon is quite commonly observed and reported in the literature, but there is no general explanation for all the described compounds.

Table 2. Photophysical parameters in the solid state for compounds **1-7**.

Comp.	Evaporated from	λ_{em} (nm)	Φ_F	CIE coordinates
1	DCM	500	0.43	(0.25, 0.46)
	ACN	500	0.24	(0.25, 0.43)
2	DCM	560 (shoulder@500)	0.24	(0.43, 0.51)
	ACN	570	0.27	(0.50, 0.47)
3	DCM	495, 560	0.26	(0.37, 0.47)
	ACN	550 (broad), 710	0.10	(0.35, 0.51)
4	DCM	595	0.14	(0.57, 0.42)
	ACN	585	0.19	(0.54, 0.46)
5	DCM	480	0.33	(0.16, 0.38)
	ACN	515, 680 (broad)	0.11	(0.28, 0.51)
6	DCM	535 (shoulder@475)	0.21	(0.29, 0.42)
	ACN	450, 515, 680 (broad)	0.13	(0.22, 0.33)
7	DCM	430, 530	0.17	(0.35, 0.46)
	ACN	450, 520	0.09	(0.28, 0.36)

Emissions from excimers (intermolecular) or exciplexes (normally intramolecular) can account for such low-energy emissions, but also emission from the locally excited S_1 in a constrained molecular organization is possible.[32] In other occasions, less common, room temperature phosphorescence is observed. For instance, recently the group of B. Z. Tang has described a molecule displaying white dual phosphorescence (from the triplet excited states T_1 and T_2) at 300 K with a solid-state Φ_F of 7.2 %.[18]

The room-temperature phosphorescence of pyrylium salts have been published, with reported emissions shifted about 40-90 nm to lower energies relative to fluorescence bands (depending on the substitution on the aromatic rings) but always in conditions of restricted movement like in poly(methyl methacrylate) (PMMA) matrices[33] or in cucurbiturils as supramolecular hosts.[34] Specifically, there is one report describing the phosphorescence of a compound related to **1** (same pyrylium core but ClO_4^- instead of BF_4^- as counterion) in PMMA which situates the emission from T_1 at 525 nm (room temperature).[33] In our case, powders obtained from DCM or ACN display emission at 500 nm at room temperature. However, this occurs in air atmosphere, which makes very unlikely that such an emission comes from a triplet state.

Li and co-workers reported a wide-shape spectrum of a diarylpyrylium salt structurally related to **1** but only interpreted the longer wavelength emission as arising from some kind of aggregated species.[28a] Most likely, excimeric emission or fluorescence from S_1 in a distorted geometry are the most plausible explanation of the emissions observed for **1-7** (**Figure 1b**). As a matter of fact, some of the studied compounds show two or even three bands, which points to some kind of combination of emissive processes. Moreover, the existence of solvates or co-crystals could play a key role in the observed emissive properties. The detailed study of all those possibilities, including X-ray diffraction studies, will be the topic of a future

research, paying special attention to the important F···H and F···C interactions that could occur due to the -CF_3 group.

The most remarkable feature of the spectra recorded in the solid state becomes apparent when the CIE coordinates for such emissions are calculated, and even more clear when looking at pictures of powders of **1-7** (**Figures 1b, 2c**), taken under UV excitation (365 nm). The solid-state emission of compounds **1-3**, **5** and **6** oscillates within the blue-green-yellow range, whereas the one of compound **4** is clearly orange. Notably, the emission of **7** is white when evaporated from ACN (Φ_F = 9%).
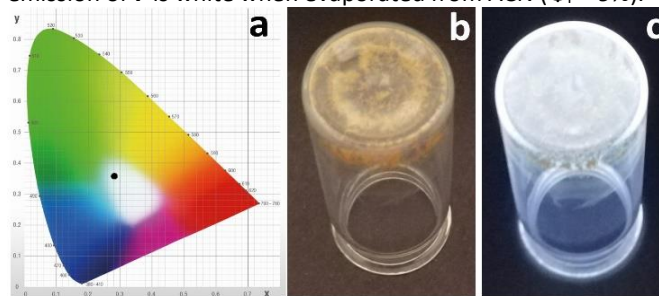

Figure 2. (a) Chromatic diagram (from Konica-Minolta) showing the coordinates (0.28, 0.36) for compound **7** evaporated from ACN (black dot in the white area); (b) picture of an inverted vial where a solution of **7** in ACN has been evaporated; (c) same vial under UV light (365 nm).

The recorded chromatic coordinates for **7** (from ACN) are (0.28, 0.36), which can be considered as white colour according to the published standards (see **Figure 2**).[17,35] This emissive property does not appear when **7** is evaporated from DCM. The results here presented highlight the importance of the solvent on the emission properties of the solids resulting after evaporation. Although parameters such as evaporation speed, temperature and initial concentration of emitter are not optimized, it is expected that fine tuning of those variables would lead, in future studies, to a better adjustment of the emission, until matching the ideal CIE coordinates for white luminescence (0.33, 0.33). In this regard, it is worth to mention that the counter-anion can have a profound influence on the emission properties of the solids, as it has been recelntly demonstrated by G. Zhang and co-workers.[36] and consequently, replacing tetrafluoroborate by other anions such as chloride, perchlorate, nitrate, etc, could help to the fine tunning of the emission in a future research.

To have an insight into the photophysical features of the studied compounds, DFT and TD-DFT calculations were performed at the B3LYP/6-31+G(d) level (see **ESI**). In the optimized structures of compounds **1-7**, the HOMO and LUMO are located over the diphenylpyrylium moiety irrespective of the solvent polarity (**Figures S11** and **S12** in **ESI**). The $S_0 \rightarrow S_1$ transitions of compounds **1-7** contributed from the HOMO $\rightarrow$ LUMO configurations can be assigned as a π,π^* transition. The wavelengths (λ_{tr}) estimated from the calculated transition energies are in the 380–450 nm wavelength region, and similar to the experimental λ_{abs} values of the lowest energy absorption bands in DCM. The magnitude of the calculated oscillator strengths (f) for the $S_0 \rightarrow S_1$ transitions is responsible for the allowed π,π^* transition. The calculated results well agree with those obtained experimentally.

In summary, by means of a straightforward reaction, seven pyrylium salts have been synthesized and characterized employing ^{1}H/^{13}C NMR, HRMS, absorption and emission spectroscopies, including solid-state fluorescence. One of the synthesized dyes displays white-light emission (CIE coordinates 0.28, 0.36) when evaporated from ACN and upon excitation with UV light. Provided the simplicity of the synthetic procedure, compound **7** could be of utility for diverse applications in the optoelectronic industry.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1   J. Li, J. Wang, H. Li, N. Song, D. Wang and B. Z. Tang, *Chem. Soc. Rev.*, 2020, **49**, 1144–1172.
2   E. Ishow, A. Brosseau, G. Clavier, K. Nakatani, P. Tauc, C. Fiorini-Debuisschert, S. Neveu, O. Sandre and A. Léaustic, *Chem. Mater.*, 2008, **20**, 6597–6599.
3   M. Shimizu, Y. Takeda, M. Higashi and T. Hiyama, *Angew. Chemie - Int. Ed.*, 2009, **48**, 3653–3656.
4   J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam and B. Z. Tang, *Chem. Rev.*, 2015, **115**, 11718–11940.
5   Z. Zhao, B. He and B. Z. Tang, *Chem. Sci.*, 2015, **6**, 5347–5365.
6   D. Li, H. Zhang, C. Wang, S. Huang, J. Guo and Y. Wang, *J. Mater. Chem.*, 2012, **22**, 4319–4328.
7   Z. Zhang, B. Xu, J. Su, L. Shen, Y. Xie and H. Tian, *Angew. Chemie - Int. Ed.*, 2011, **50**, 11654–11657.
8   (a) B. Tang, C. Wang, Y. Wang and H. Zhang, *Angew. Chemie - Int. Ed.*, 2017, **56**, 12543–12547; (b) R. Huang, B. Liu, C. Wang, Y. Wang and H. Zhang, *J. Phys. Chem. C*, 2018, **122**, 10510–10518.
9   H. Rabbani-Haghighi, Ś. Forget, Ś. Chńais, A. Siove, M. C. Castex and E. Ishow, *Appl. Phys. Lett.*, 2009, **95**, 2007–2010.
10 B. Liu, Q. Di, W. Liu, C. Wang, Y. Wang and H. Zhang, *J. Phys. Chem. Lett.*, 2019, **10**, 1437–1442.
11 J. Malinge, C. Allain, A. Brosseau and P. Audebert, *Angew. Chemie - Int. Ed.*, 2012, **51**, 8534–8537.
12 E. Ferreira Molina, N. A. Martins de Jesus, S. Paofai, P. Hammer, M. Amela-Cortes, M. Robin, S. Cordier and Y. Molard, *Chem. - A Eur. J.*, 2019, **25**, 15248–15251.
13 Q. Y. Yang and J. M. Lehn, *Angew. Chemie - Int. Ed.*, 2014, **53**, 4572–4577.
14 Z. Xie, C. Chen, S. Xu, J. Li, Y. Zhang, S. Liu, J. Xu and Z. Chi, *Angew. Chemie - Int. Ed.*, 2015, **54**, 7181–7184.
15 N. N. Zhang, C. Sun, X. M. Jiang, X. S. Xing, Y. Yan, L. Z. Cai, M. S. Wang and G. C. Guo, *Chem. Commun.*, 2017, **53**, 9269–9272.
16 B. Li, J. Lan, D. Wu and J. You, *Angew. Chemie - Int. Ed.*, 2015, **54**, 14008–14012.
17 D. Tu, P. Leong, S. Guo, H. Yan, C. Lu and Q. Zhao, *Angew. Chemie - Int. Ed.*, 2017, **56**, 11370–11374.
18 Z. He, W. Zhao, J. W. Y. Lam, Q. Peng, H. Ma, G. Liang, Z. Shuai and B. Z. Tang, *Nat. Commun.*, 2017, **8**, 1–7.
19 J. Wang, X. Gu, H. Ma, Q. Peng, X. Huang, X. Zheng, S. H. P. Sung, G. Shan, J. W. Y. Lam, Z. Shuai and B. Z. Tang, *Nat. Commun.*, 2018, **9**, 1–9.
20 (a) M. Shimizu and T. Hiyama, *Chem. - An Asian J.*, 2010, **5**, 1516–1531; (b) V. K. Praveen, C. Ranjith and N. Armaroli, *Angew. Chemie - Int. Ed.*, 2014, **53**, 365–368; (c) D. Li, J. Wang and X. Ma, *Adv. Opt. Mater.*, 2018, **6**, 1–27; D) M. K. Bera, P. Pal and S. Malik, *J. Mater. Chem. C*, 2020, **8**, 788–802.
21 (a) M. A. Miranda and H. García, *Chem. Rev.*, 1994, **94**, 1063–1089; (b) M. A. Miranda, M. A. Izquierdo and F. Galindo, *Org. Lett.*, 2001, **3**, 1965–1966; (c) N. A. Romero and D. A. Nicewicz, *Chem. Rev.*, 2016, **116**, 10075–10166.
22 T. Y. Ohulchanskyy, M. K. Gannon, Y. Mao, A. Skripchenko, S. J. Wagner, P. N. Prasad and M. R. Detty, *J. Phys. Chem. B*, 2007, **111**, 9686–9692.
23 A. Beltrán, M. Isabel Burguete, D. R. Abánades, D. Pérez-Sala, S. V. Luis and F. Galindo, *Chem. Commun.*, 2014, **50**, 3579–3581.
24 (a) D. Jiménez, R. Martínez-Máñez, F. Sancenón, J. V. Ros-Lis, A. Benito and J. Soto, *J. Am. Chem. Soc.*, 2003, **125**, 9000–9001; (b) M. Comes, M. Dolores Marcos, R. Martínez-Máñez, F. Sancenón, J. Soto, L. A. Villaescusa, P. Amorós and D. Beltrán, *Adv. Mater.*, 2004, **16**, 1783–1786; (c) F. García, J. M. García, B. García-Acosta, R. Martínez-Máñez, F. Sancenón and J. Soto, *Chem. Commun.*, 2005, 2790–2792.
25 A. Beltrán, M. I. Burguete, S. V. Luis and F. Galindo, *European J. Org. Chem.*, 2017, **32**, 4864–4870.
26 A. Beltrán, M. I. Burguete, S. V. Luis and F. Galindo, *RSC Adv.*, 2016, **6**, 56064–56068.
27 S. Harmsen, M. A. Bedics, M. A. Wall, R. Huang, M. R. Detty and M. F. Kircher, *Nat. Commun.*, 2015, **6**, 1-9.
28 (a) D. Li, J. Zhang and M. Anpo, *Opt. Mater. (Amst).*, 2005, **27**, 671–673; (b) G.-L. Gong, Wei-Tao; Qian, Xiao-min; Wang, Fu-Rui; Lin, Yuan; Ning, *Heteroat. Chem.*, 2013, **24**, 66–71; (c) L. Yang, J. Ye, Y. Gao, D. Deng, W. Gong, Y. Lin and G. Ning, *Tetrahedron Lett.*, 2013, **54**, 2967–2971; (d) I. E. Serdiuk, *J. Phys. Chem. C*, 2018, **122**, 18615-18620; (e) P. K. Bhowmik, C. I. Lee, J. J. Koh, H. Han, A. Jubair, V. Kartazaev and S. K. Gayen, *J. Mol. Struct.*, 2020, **1202**, 127325.
29 T.A. Markina and N.N Boiko, *Chem. Heterocycl. Compd.*, 1985, 138–139.
30 G. Haucke, P. Czerney and F. Cebulla, *Ber. . Bun. Phys. Chem.*, 1992, **96**, 880–886.
31 (a) H. Zhang, Z. Zhang, K. Ye, J. Zhang and Y. Wang, *Adv. Mater.*, 2006, **18**, 2369–2372; (b) N. Oka, F. Ito, Y. Haketa, H. Maeda, T. Miyano, N. Tohnai, S. Ito, H. Miyasaka and S. Ozeki, *Chem. - A Eur. J.*, 2018, **24**, 4343–4349; (c) Y. Chen, Z. Peng, Y. Tao, Z. Wang, P. Lu and Y. Wang, *Dye. Pigment.*, 2019, **161**, 44–50; (d) M. Khorloo, Y. Cheng, H. Zhang, M. Chen, H. H. Y. Sung, I. D. Williams, J. W. Y. Lam and B. Z. Tang, *Chem. Sci.*, 2020, **11**, 997–1005.
32 (a) H. Sasabe, K. Sasaki, M. Mamiya, Y. Suwa, T. Watanabe, N. Onuma, K. Nakao, M. Yamaji and J. Kido, *Chem. - An Asian J.*, 2017, **12**, 2299–2303; (b) M. Yamaji, S. I. Kato, K. Tomonari, M. Mamiya, K. Goto, H. Okamoto, Y. Nakamura and F. Tani, *Inorg. Chem.*, 2017, **56**, 12514–12519; (c) M. Yamaji and H. Okamoto, *J. Photochem. Photobiol. A Chem.*, 2018, **360**, 204–209; (d) M. Mamiya, Y. Suwa, H. Okamoto and M. Yamaji, *Photochem. Photobiol. Sci.*, 2016, **15**, 278–286; (e) M. Yamaji, K. Tomonari, K. Ikuma, K. Goto, F. Tani and H. Okamoto, *Photochem. Photobiol. Sci.*, 2019, **18**, 2884–2892.
33 V. Wintgens, J. Pouliquen, J. Kossanyi, J. L. R. Williams and J. C. Doty, *Polym. Photochem.*, 1985, **6**, 1–20.
34 P. Montes-Navajas, L. Teruel, A. Corma and H. Garcia, *Chem. - A Eur. J.*, 2008, **14**, 1762–1768.
35 T. Ghosh and E. Prasad, *J. Phys. Chem. C*, 2015, **119**, 2733–2742.
36 G. Zhang, X. Zhang, L. Kong, S. Wang, Y. Tian, X. Tao and J. Yang, Sci. Rep. 2016, 6, 37609.