

# Photophysics and Electrochemistry of Some Thione Far-Red/Near-IR Triplet Emitters

Rachel C. Evans · Peter Douglas ·  
Christopher J. Winscom

Received: 6 June 2008 / Accepted: 2 July 2008 / Published online: 6 August 2008  
© Springer Science + Business Media, LLC 2008

**Abstract** The photophysics and cyclic voltammetry of two novel phosphorescent thiones, 2,2-dimethyl-indan-1-one-3-thione (**DMIKT**) and 2,2-dimethyl-indan-1,3-dithione (**DMIDT**), and three known phosphorescent thiones, 4*H*-pyran-4-thione (**PT**), 4*H*-1-benzopyran-4-thione (**BPT**) and 2,2-dimethylindan-1-thione (**DMIT**), have been characterised and compared. The phosphorescence emission of **DMIT**, **DMIKT** and **DMIDT** extends from the red into the near-IR spectral region. The additional carbonyl or thione group of **DMIKT** and **DMIDT** causes a significant shift in the emission maxima to 680 nm compared to that of **DMIT**, at 637 nm, in perfluorinated hydrocarbons. In acetonitrile the emission maxima of **DMIKT** and **DMIDT** are at 696 and 706 nm, respectively, and the spectra show vibronic bands which extend out beyond 850 nm. There is a significant reduction in triplet lifetime along this series (from 44 ( $\pm 2$ )  $\mu\text{s}$  (**DMIT**) to 10 ( $\pm 0.8$ )  $\mu\text{s}$  (**DMIKT**) in perfluorinated solvents, and 8.6 ( $\pm 0.5$ ) (**DMIT**), 1.3 ( $\pm 0.5$ ) (**DMIKT**) and 0.35 ( $\pm 0.07$ )  $\mu\text{s}$  (**DMIDT**) in acetonitrile),

as well as a reduction in the rate constant for ground-state quenching of the triplet, (from 9.8 ( $\pm 0.9$ ) to 3.5 ( $\pm 0.6$ ) and 1.3 ( $\pm 0.2$ )  $\times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  for the same compounds). The addition of the C=O or C=S groups also causes a decrease in phosphorescence quantum yield with the highest emission quantum yield obtained for **DMIT** ( $\Phi_{\text{p}}=0.149$  ( $\pm 0.015$ )). Electrochemical studies show that while **PT** and **BPT** exhibit irreversible redox behaviour, **DMIT**, **DMIKT** and **DMIDT** all show at least one reversible reduction wave attributed to a one-electron process centred on the C=S moiety. The suitability of these lumophores for use in OLEDs is discussed.

**Keywords** Thiones · Phosphorescence · Triplet emitters · Infrared · OLED

## Introduction

In recent years room temperature (RT) triplet emitters have become of significant interest for use in organic light-emitting diodes (OLEDs), which are emerging as the leading technology for the new generation of flat panel displays [1, 2]. The use of phosphorescent materials as the emissive component has the potential to improve the luminous efficiency by up to a factor of four compared to purely fluorescent dopant-based devices [3, 4]. In general, the triplet emitters employed are neutral complexes of the second and third row transition metals, such as Ir(III), Os(II) and Pt(II) [5, 6]. These complexes frequently exhibit high RT phosphorescence quantum yields and short emission lifetimes, due to efficient spin-orbit coupling as a consequence of the heavy atom effect. However, the use of a metal complex triplet emitter is by no means a fundamental requirement for this technology; any neutral

R. C. Evans (✉) · P. Douglas  
Department of Chemistry,  
University of Wales Swansea,  
Singleton Park,  
Swansea SA2 8PP, UK  
e-mail: rachelcevans@yahoo.co.uk

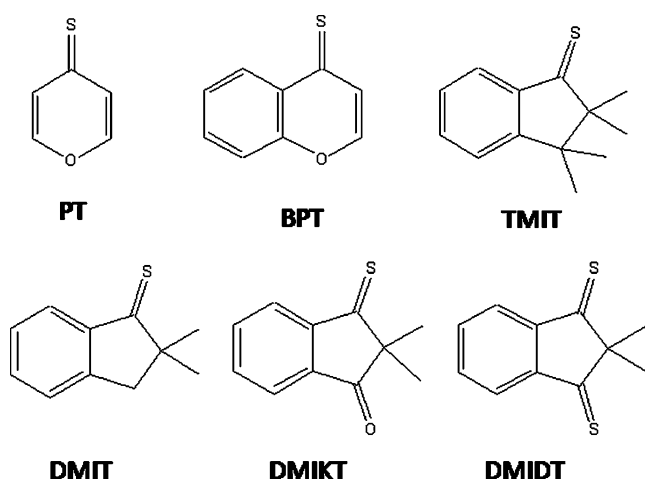
C. J. Winscom  
Kodak European Research,  
332 Science Park, Milton Road,  
Cambridge CB4 0FW, UK

*Present address:*  
R. C. Evans  
Department of Chemistry,  
University of Coimbra,  
Rua Larga,  
Coimbra 3004-535, Portugal

molecule exhibiting RT phosphorescence could in principle be used.

In an attempt to follow a new research direction, our approach has been to evaluate the potential of known RT triplet emitters for OLED technology, and in particular, non-metallic compounds. Aromatic thiones are known to exhibit fascinating photophysical properties, including fluorescence from the  $S_2$  state [7–9], thermally-activated delayed fluorescence from the  $S_1$  state [8–10], as well as RT phosphorescence from the  $T_1$  state [9–14]. Aromatic thiones have already been investigated for several applications, including their use as luminescent probes in micellar studies [15], and for the determination of the polarity of microenvironments, for example in cyclodextrin cavities [16, 17], as well as new efficient photosensitisers of singlet oxygen [18]. However, to our knowledge, there have been no studies into the suitability of aromatic thiones as triplet emitters for OLED devices. This is surprising since, on paper, phosphorescent aromatic thiones satisfy several of the requirements for OLED technology, namely (a) intense RT phosphorescence; (b) emission lifetimes in the microsecond regime; and (c) satisfactory phosphorescence quantum yields. Moreover, other workers have recently discussed the potential of an emissive tellurium analogue, telluroxanthone, for OLED applications [19].

Here we describe the synthesis, characterisation, and the photophysical and electrochemical properties of the aromatic thiones shown in Fig. 1. *4H*-pyran-4-thione (**PT**) and *4H*-1-benzopyran-4-thione (**BPT**) have been extensively studied by other workers and there is comprehensive absorption, emission and lifetime data available for the  $S_1$ ,  $S_2$  and  $T_1$  states of these compounds [7–13]. In addition to blue  $S_2 \rightarrow S_0$  fluorescence, these compounds exhibit intense phosphorescence in RT degassed solution in the red spectral region with phosphorescence quantum yields as high as  $\Phi_p = 0.47$  [11] and 0.13 [12] reported for **PT** and **BPT**,



**Fig. 1** Structures of the aromatic thiones discussed in this study

respectively, on direct excitation into the  $T_1$  band. However, to the best of our knowledge, no electrochemical data have been reported for these compounds. The photophysics of 2,2,3,3-tetramethylindan-1-thione (**TMIT**) have also been intensively studied [8, 10, 12, 14]. The dimethylated analogue discussed here, 2,2-dimethylindan-1-thione (**DMIT**), has been previously synthesised [20, 21], but there have been no reports of its photophysical or photochemical characteristics. The related 2,2-dimethylindan-1-one-3-thione (**DMIKT**) and 2,2-dimethylindan-1,3-dithione (**DMIDT**) are new compounds and were chosen in order to study the effect of an additional thione group on the photophysical properties of this series.

## Experimental

### Materials

All solvents used for synthesis were at least reagent-grade and used without further purification. Solvents for spectroscopic measurements were treated as follows. Acetonitrile and cyclohexane (AnalR grade), purchased from Fisher Scientific and perfluoro-1,3-dimethylcyclohexane (PF-1,3-DMCH), purchased from Aldrich, were fractionally distilled to give solvents >99% pure by GC. None of the solvents exhibited any detectable emission under the conditions used. The ketone precursors *4H*-pyran-4-one and *4H*-chromen-4-one (for **PT** and **BPT** respectively) were purchased from Aldrich and used as received. Indan-1-one and indan-1,3-dione were purchased from Aldrich and dimethylated in the 2' position with NaH/MeI according to published methods to yield the 2,2-dimethylindan-1-one [22] and 2,2-dimethylindan-1,3-dione ketone precursors respectively [23].

Thiones were prepared by sulphurisation of the corresponding carbonyl compound using the method previously described by Lawesson et al. [24, 25]. A solution of the carbonyl starting material (1 eq.) and Lawesson's reagent [2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulphide] (0.54 eq.) in anhydrous toluene (40 ml) were heated at reflux under nitrogen (2–5 h). For the dithione **DMIDT**, a second batch of Lawesson's reagent (0.54 eq.) was added to the reaction mixture after 3 h reflux. The reaction was monitored by TLC and stopped after most of the starting material had been consumed. This reaction resulted in the formation of a significant quantity of side-product, which has also been reported by other workers, and the low thione yields are attributed to this [18]. Once the reaction had reached completion, the solvent was removed and the residue was chromatographed on a silica gel column with toluene/hexane (1:3) as the eluent to yield the thioketone product. In addition to chromatographic purification, the crystalline thiones **PT**, **BPT** and **DMIKT** were

further purified by vacuum sublimation (75 °C). No thermal degradation of the sample was observed at this temperature and purification yields were *ca.* 80%. Analysis of the sublimed samples by GC revealed the materials were >99% pure. Since vacuum sublimation is the favoured deposition method for small-molecule OLEDs, this stability is worthy of note. Following preparation, all thiones were stored in a freezer in the dark until required.

All compounds were characterised using  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, infrared spectroscopy (IR), and low-resolution electron ionisation (EI) and chemical ionisation (CI) mass spectrometry. Accurate mass spectroscopy was obtained for all thiones with the exception of **DMIDT**, which proved to be too unstable. Characterisation of the known compounds, **PT** [26], **BPT** [26], and **DMIT** [20, 21], was in good agreement with the literature. The characterisation of the novel compounds 2,2-dimethyl-indan-1-one-3-thione (**DMIKT**) and 2,2-dimethyl-indan-1,3-dithione (**DMIDT**) is summarised below.

**DMIKT** Purple crystals, 89 mg, 20% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  [ppm]: 1.51 (s, 6H), 7.78–7.82 (t,  $J=16.3$  Hz, 1H), 7.88–7.95 (m,  $J=16.1$  Hz, 2H), 8.10–8.15 (d,  $J=8.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  [ppm]: 20.68, 24.53, 53.84, 123.72, 124.17, 135.89, 136.28, 206.85, 245.96; MS  $m/z$  (relative intensity): 190.0 ( $\text{M}^+$ , 100), 147.0 (63), 128.0 (74), 115.0 (35), 69.0 (31); HRMS:  $\text{M}^+$  (calc.) 190.0447,  $\text{M}^+$  (meas.) 190.0446; IR (neat): 2,974 (m), 1,703 (s), 1,592 (m), 1,505 (m), 1,286 (s), 1,197 (m), 1,005 (m), 795 (m), 721 (s)  $\text{cm}^{-1}$ .

**DMIDT** Blue liquid 26 mg, 18% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  [ppm]: 1.40 (s, 6H), 7.71–7.73 (dd,  $J=6.2$  Hz, 2H), 7.95–7.98 (m,  $J=6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  [ppm]: 28.05, 70.61, 124.04, 135.83, 145.74, 247.34; MS  $m/z$  (relative intensity): 206.0 ( $\text{M}^+$ , 23), 159.0 (38), 127.8 (76), 115.0 (56), 64.0 (100); IR (neat): 2,974 (m), 1,702 (m), 1,593 (m), 1,504 (m), 1,284 (s), 1,197 (s), 1,006 (m), 795 (m), 722 (s)  $\text{cm}^{-1}$ .

## Methods

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were recorded on a 400 MHz Bruker AC spectrometer. Mass spectra were recorded at the EPSRC Mass Spectrometry Centre. Low resolution EI/CI measurements were carried out using a VG analytical Quattro II triple quadrupole mass spectrometer. High resolution electron ionisation mass spectrometry (HRMS) accurate mass peak match of the molecular ion ( $\text{M}^+$ ) was measured against the reference compound perfluorotributylamine. IR spectroscopy was performed using a Perkin

Elmer “Spectrum-one” FT-IR spectrophotometer. UV–vis absorption spectra were recorded on a Hewlett Packard 8452A diode array UV–visible spectrometer in either 1 or 4 cm quartz cuvettes depending on the sample concentration. Molar extinction coefficients were determined for each compound from a Beer–Lambert plot of the sample absorbance at concentrations in the range  $10^{-4}$ – $10^{-6}$  mol  $\text{dm}^{-3}$ . Steady-state emission spectra and emission quantum yields were measured at 295K in 1 cm long-neck sealed quartz cuvettes using  $90^\circ$  geometry on a Perkin Elmer MPF-44E fluorescence spectrometer. All solutions were purged with  $\text{N}_2$  for 20 min prior to measurement. All emission spectra were corrected using correction data obtained with rhodamine B and methylene blue as quantum counters for wavelengths out to 720 nm [27], beyond which the response was estimated from the manufacturer’s photomultiplier response data. The emission quantum yield,  $\Phi_x$ , of thione  $x$ , was measured by relating it to a reference standard,  $R$ , of known quantum yield,  $\Phi_R$ , using the following equation [28]:

$$\Phi_x = \Phi_R \cdot \frac{A_R}{A_x} \cdot \frac{I_x}{I_R} \cdot \left( \frac{\eta_x}{\eta_R} \right)^2 \cdot \frac{P_R}{P_x} \quad (1)$$

where  $A$  is the fraction of light absorbed at the excitation wavelength,  $I$  is the integrated emission intensity corrected for the instrument response,  $\eta$  is the refractive index of the solvent and  $P$  is the optical excitation power i.e. the intensity at the excitation wavelength, and  $x$  and  $R$  refer to the sample and reference respectively. Yields were measured in PF-1, 3-DMCH at 295 K using tetraphenylporphyrin as a red emitting reference standard (**TPP**, Aldrich,  $\Phi_{\text{em}}=0.11$  in toluene on excitation at 514 nm) [29]. The sample and the standard solutions were matched to have an identical absorbance at the excitation wavelength. Quantum yields were measured at low thione concentrations (*ca.*  $10^{-6}$  mol  $\text{dm}^{-3}$ ) to minimise the contribution of thione self-quenching and then emission quantum yields at infinite dilution,  $\Phi_p$ , were calculated from the kinetic data (Table 2) according to:

$$\Phi_p = \Phi_x \cdot \frac{(k_0 + k_{\text{SQ}}[\text{Thione}])}{k_0} \quad (2)$$

where [Thione] is the concentration of the sample for which the experimental quantum yield,  $\Phi_x$ , was determined, (typically between  $5$ – $9 \times 10^{-7}$  mol  $\text{dm}^{-3}$ ). Using **TPP** as standard gives  $\Phi_x=0.28$  for **PT** at  $5 \times 10^{-7}$  mol  $\text{dm}^{-3}$ ; which, when combined with kinetic data, gives  $\Phi_p=0.35$  at infinite dilution, in good agreement with previous literature ( $\Phi_p=0.33$  ( $\text{S}_2$ ), see Table 2) [11]. The error in quantum yields is estimated to be *ca.* 10%.

Phosphorescence lifetime measurements were carried out at 295 K using the third harmonic (355 nm) of a Q-switched Nd/YAG Spectron laser for excitation and an Applied Photo-

**Table 1** UV–vis absorption maxima ( $\lambda$ ) and extinction coefficients ( $\epsilon$ ) in different solvents

	PF-1,3-DMCH	Cyclohexane	MeCN
	$\lambda/\text{nm}$ ( $\epsilon/10^4 \text{ mol}^{-1}$ $\text{dm}^3 \text{ cm}^{-1}$ )	$\lambda/\text{nm}$ ( $\epsilon/10^4 \text{ mol}^{-1}$ $\text{dm}^3 \text{ cm}^{-1}$ )	$\lambda/\text{nm}$ ( $\epsilon/10^4 \text{ mol}^{-1}$ $\text{dm}^3 \text{ cm}^{-1}$ )
<b>PT</b>	330 (1.6±0.1)	329 (1.2±0.1)	340 (1.4±0.1)
<b>BPT</b>	359 (1.8±0.1)	275 (0.8±0.2)	278 (0.9±0.2)
		360 (1.4±0.2)	373 (1.5±0.1)
<b>DMIT</b>	318 (0.9±0.1)	311 (1.1±0.1)	315 (1.1±0.1)
	328 (1.3±0.2)	324 (1.1±0.1)	330 (1.0±0.1)
<b>DMIKT</b>	296 (1.8±0.1)	306 (1.1±0.1)	294 (0.6±0.1), 307 (1.1±0.1)
	302 (1.6±0.1)		322 (1.1±0.1)
<b>DMIDT</b>	–	298 (0.3±0.1)	306 (0.3±0.1)
		330 (0.2±0.1)	331 (0.4±0.1)
2,2-Dimethylindan-1-one	–		286 (0.3±0.1), 294 (0.2 ± 0.1)
			306 (0.1±0.1)
2,2-Dimethylindan-1,3-dione			246 (0.9±0.2), 290 (0.6 ± 0.2), 301 (0.6±0.2)

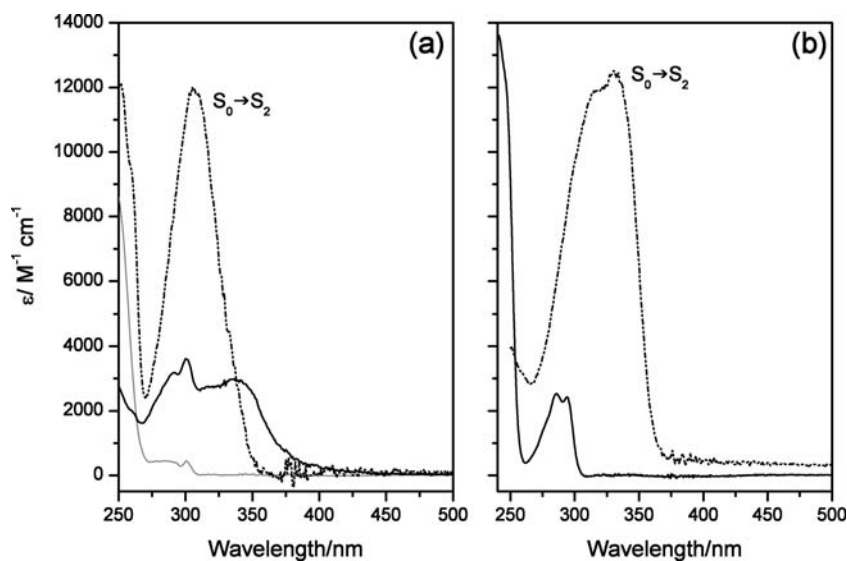
physics laser kinetic spectrometer for detection. The data was recorded using a LeCroy 9304 AM Quad 200 MHz digital storage oscilloscope before transfer to a PC for analysis. The uncertainty in the measured lifetimes is *ca.* 5%.

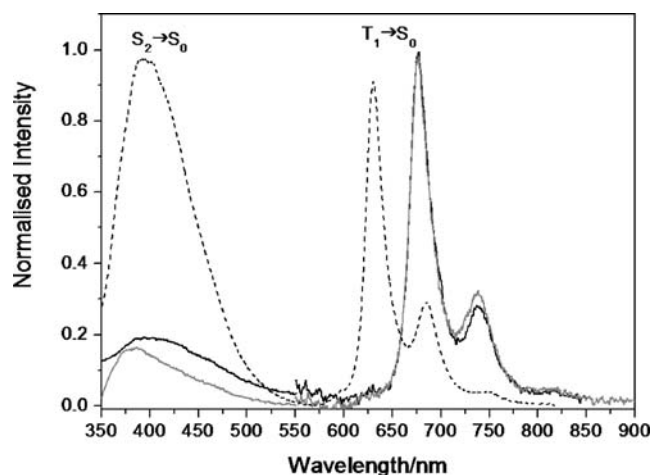
Cyclic voltammetry was performed using an Autolab PGSTAT30 potentiostat system. Samples were dissolved in MeCN with  $0.1 \text{ mol dm}^{-3}$   $[\text{NBu}_4][\text{PF}_6]$  in MeCN as the supporting electrolyte. Solutions were purged with nitrogen gas prior to each scan. A three electrode system was employed using a platinum working and auxiliary electrode and a  $\text{Ag}/\text{Ag}^+$  ( $0.01 \text{ mol dm}^{-3}$   $\text{AgNO}_3$  in MeCN) reference electrode. The scan rate was  $100 \text{ mV s}^{-1}$ . The voltgrams were referenced to a ferrocene–ferrocenium couple as the standard ( $E^0=0.42 \text{ vs. SCE}$ ).

## Results

The RT ground state absorption properties of the thiones in several solvents are collected in Table 1. All show a red-shift in the absorption maximum with increasing solvent polarity. Figure 2 displays the absorption spectra for **DMIT**, **DMIKT** and **DMIDT** and the parent ketones, 2,2-dimethylindan-1-one and 2,2-dimethylindan-1,3-dione, in cyclohexane. The observed absorption spectra contain two well-separated band systems in the region 250–400 nm, which are characteristic of aromatic thiones and are assigned to intense  $S_0 \rightarrow S_3$  and  $S_0 \rightarrow S_2$  symmetry-allowed absorption bands due to a singlet  $\pi \rightarrow \pi^*$  electron promotion largely localized on the C=S moiety [7, 9]. A bathochromic

**Fig. 2** UV–visible absorption spectra of **a** **DMIKT** (dashed line), **DMIDT** (black solid line) and 2,2-dimethylindan-1,3-dione (grey solid line) and **b** **DMIT** (dashed line) and 2,2-dimethylindan-1-one (solid line). All spectra recorded in cyclohexane at 295 K





**Fig. 3** Normalised emission spectra (295 K, under  $N_2$ ) of **DMIT** ( $\lambda_{\text{ex}}=310$  nm, *dashed line*), **DMIKT** ( $\lambda_{\text{ex}}=304$  nm, *black solid line*) and **DMIDT** ( $\lambda_{\text{ex}}=300$  nm, *grey solid line*) in PF-1,3-DMCH

shift of *ca.* 10–20 nm is observed on changing from the parent ketone to the corresponding thione [18]. Linear Beer–Lambert plots were obtained for all compounds in all solvents in the concentration range studied ( $10^{-6}$ – $10^{-5}$  mol  $\text{dm}^{-3}$ ). With the exception of **DMIDT**, extinction coefficients ( $\epsilon$ ) are of the order of  $10^4$  mol $^{-1}$  dm $^3$  cm $^{-1}$  and are *ca.* five to ten times larger for thiones compared to the parent ketones [18].

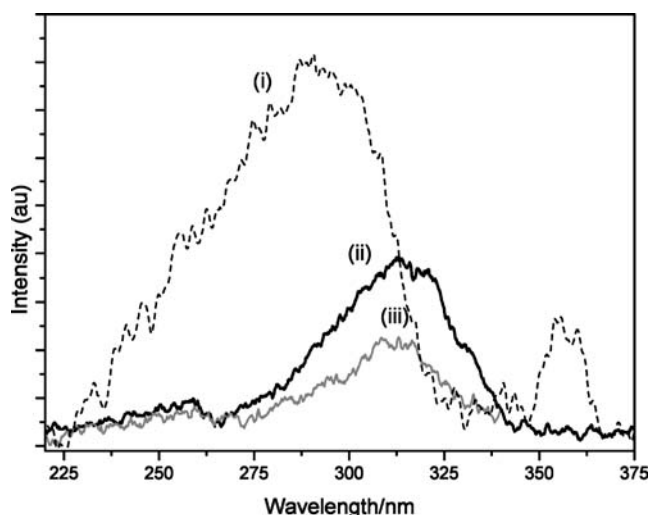
The RT emission spectra for **DMIT**, **DMIKT** and **DMIDT** are shown in Fig. 3. RT luminescence band maxima,

phosphorescence quantum yields, phosphorescence lifetimes and self-quenching rate-constants are collected in Table 2. Following excitation into the  $S_2$  band, the thiones exhibit both  $S_2 \rightarrow S_0$  fluorescence and  $T_1 \rightarrow S_0$  phosphorescence in deaerated RT solution. This is in agreement with the luminescence behaviour previously reported for **PT** and **BPT** [8, 9]. In deaerated solution the  $S_2 \rightarrow S_0$  fluorescence and  $T_1 \rightarrow S_0$  phosphorescence bands of **DMIT** are of comparable intensity. The  $S_2 \rightarrow S_0$  fluorescence bands of **DMIKT** and **DMIDT** are located in the region of 360–400 nm, which is considerably red-shifted compared to the parent ketone fluorescence, which has a maximum at *ca.* 315 nm (not shown). The  $S_2 \rightarrow S_0$  fluorescence band observed for **DMIKT** is broader and extends further into the UV region than the corresponding emission band observed for **DMIDT**, with full-width-at-half-maxima (FWHM) of *ca.* 8,000 and 5,000  $\text{cm}^{-1}$  respectively. For both **DMIKT** and **DMIDT** the  $S_2 \rightarrow S_0$  fluorescence is considerably weaker than the phosphorescence emission band. For all thiones the  $T_1 \rightarrow S_0$  phosphorescence band is split into a number of broad, well-resolved vibrational features, which is typical of aromatic thiones in non-polar media [8, 9, 11]. The phosphorescence is considerably quenched in the presence of oxygen, such that, the  $S_2 \rightarrow S_0$  fluorescence band dominates the emission spectra in aerated solutions. A red-shift of *ca.* 45 nm is observed in the emission maximum of the  $T_1 \rightarrow S_0$  (0,0) phosphorescence band on changing from **DMIT** to **DMIKT** or **DMIDT**. Since little distinction can be made

**Table 2** Luminescence data for aromatic thiones in solution (295 K)

Thione	Solvent	$\lambda_{\text{em}}(S_2)/\text{nm}$	$\lambda_{\text{em}}(T_1)/\text{nm}$	$\Phi_p$	$k_0/10^4 \text{ s}^{-1}$	$\tau_0/\mu\text{s}$	$k_{\text{SQ}}/10^9 \text{ M}^{-1} \text{ s}^{-1}$	Refs.
<b>PT</b>	PF-1, 3-DMCH	382	598, 641	0.35	2.33 ( $\pm 0.25$ )	43 ( $\pm 4$ )	13.6 ( $\pm 0.6$ )	This work [11]
				( $\pm 0.04$ ) ( $S_2$ ) 0.47 ( $\pm 0.07$ ) ( $T_1$ )				
<b>BPT</b>	PF-1, 3-DMCH	444	630	0.076	6.35 ( $\pm 0.50$ )	16 ( $\pm 2$ )	6.9 ( $\pm 0.9$ )	[8, 12]
				( $\pm 0.010$ ) ( $S_2$ ) 0.13 ( $\pm 0.03$ ) ( $T_1$ )				
<b>DMIT</b>	Cyclohexane	394	631	–	2.16 ( $\pm 0.13$ )	46 ( $\pm 2$ )	6.0 ( $\pm 0.4$ )	This work
	MeCN	395	639	–	11.60 ( $\pm 0.31$ )	8.6 ( $\pm 0.5$ )	9.8 ( $\pm 0.9$ )	
	PF-1, 3-DMCH	394	637	0.149 ( $S_2$ )	2.28 ( $\pm 0.18$ )	44 ( $\pm 2$ )	4.6 ( $\pm 0.2$ )	
<b>DMIKT</b>	Cyclohexane	395	678	–	18.32 ( $\pm 0.27$ )	5.5 ( $\pm 0.5$ )	1.7 ( $\pm 0.1$ )	This work
	MeCN	404	696	–	77.38 ( $\pm 0.28$ )	1.3 ( $\pm 0.5$ )	3.5 ( $\pm 0.6$ )	
	PF-1, 3-DMCH	400	680	0.018 ( $S_2$ )	9.93 ( $\pm 0.35$ )	10.0 ( $\pm 0.8$ )	2.3 ( $\pm 0.7$ )	
<b>DMIDT</b>	MeCN	385	706	–	289 ( $\pm 35$ )	0.35 ( $\pm 0.07$ )	1.3 ( $\pm 0.2$ )	This work
	PF-1, 3-DMCH	–	680	–	–	–	–	

$\lambda_{\text{em}}(S_2)$  and  $\lambda_{\text{em}}(T_1)$  are the emission maxima of the  $S_2 \rightarrow S_0$  fluorescence and  $T_1 \rightarrow S_0$  phosphorescence bands respectively,  $\Phi_p$  is the phosphorescence quantum yield from excitation into either the second singlet ( $S_2$ ) or first triplet ( $T_1$ ) states,  $k_0$  and  $\tau_0$  are the decay rate constant and corresponding triplet lifetime at infinite dilution and  $k_{\text{SQ}}$  is the rate constant for self-quenching



**Fig. 4** Excitation spectra (295 K, under  $N_2$ ) of (i) 2,2-dimethylindan-1,3-dione ( $\lambda_{em}=388$  nm) and (ii) **DMIKT** ( $\lambda_{em}=396$  nm ( $T_1 \rightarrow S_0$ )); and (iii) **DMIDT** ( $\lambda_{em}=680$  nm ( $T_1 \rightarrow S_0$ )) in PF-1,3-DMCH. The relative intensities of these bands can not be compared due to the different instrumental conditions used for each sample

between the phosphorescence emission observed for **DMIKT** and **DMIDT**, this suggests that only one C=S moiety is involved in the  $^3(n, \pi^*)$  electronic state responsible for this emission in both compounds.

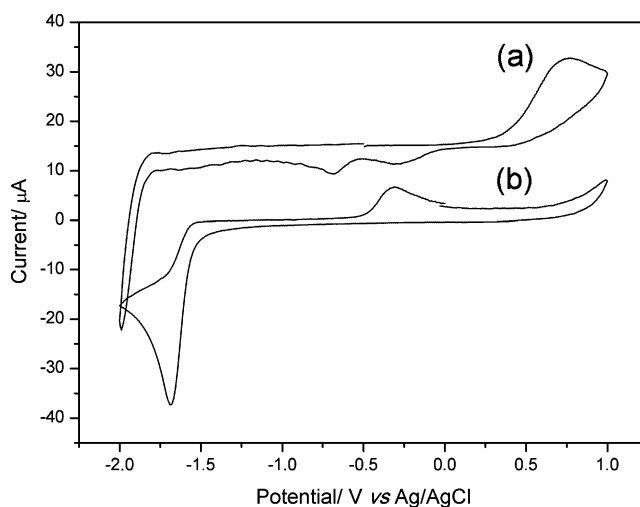
Figure 4 shows the excitation spectra obtained for **DMIKT**, **DMIDT** and the parent ketone 2,2-dimethylindan-1,3-dione. **DMIKT** and **DMIDT** show similar spectra on detection in the  $T_1 \rightarrow S_0$  transition, with an excitation band with a maximum at *ca.* 314 nm. However, while **DMIKT** is reasonably photostable **DMIDT** undergoes considerable photodegradation, observed as a significant decrease in the phosphorescence emission intensity with time, presumably as a consequence of photooxidation back to the parent ketone. (Note that the band observed between *ca.* 350–370 nm in the excitation spectrum of 2,2-dimethylindan-1,3-dione is probably associated with Raman scattering.)

Triplet-excited thiones are known to undergo efficient self-quenching by ground-state molecules [8, 9]. This is the case for all thiones used in this study in all solvents investigated. The intrinsic lifetime of the  $T_1$  state can therefore only be approached when measurements are made in very dilute solutions ( $<10^{-7}$  mol  $dm^{-3}$ ) [9]. The triplet emission lifetime and decay rate constant at infinite dilution,  $\tau_0$  and  $k_0$ , and the bimolecular rate constant for self-quenching,  $k_{SQ}$ , were determined from the linear variation of the observed rate constant,  $k_{obs}$ , as a function of thione concentration, according to Eq. 3. The emission decay traces were monoexponential for all thiones across the concentration range studied ( $10^{-4}$ – $10^{-6}$  mol  $dm^{-3}$ ).

$$k_{obs} = k_0 + k_{SQ}[\text{Thione}]. \quad (3)$$

The values of the self-quenching rate constants,  $k_{SQ}$ , obtained in this way are collected in Table 2 and are of a similar order of magnitude to those previously reported in the literature [8, 12]. However, it is interesting to note that while a near diffusion-controlled interaction between  $T_1$  and  $S_0$  is generally observed for those thiones with phosphorescence maxima in the 630–640 nm region, for those with emission maxima in the far red/near IR, i.e. 680–710 nm, self quenching is much less efficient, with  $k_{SQ}$  as much as an order of magnitude less than that for full diffusion control. Triplet lifetimes at infinite dilution,  $\tau_0$ , range between *ca.* 1–40  $\mu s$  and show considerable solvent dependence. Triplet lifetimes decrease significantly on descending the series of thiones **DMIT**, **DMIKT** and **DMIDT**. This coincides with a decrease in the  $T_1$ – $S_0$  energy gap, indicating that non-radiative  $T_1$  decay pathways become more important as the triplet energy is reduced with the addition of further C=O and/or C=S moieties. This is in agreement with the lower phosphorescence quantum yield measured for **DMIKT** compared to **DMIT**. For all thiones the intrinsic triplet decay rate constants  $k_0$  are significantly faster in MeCN, indicating that the solvent is important in the unimolecular triplet deactivation process. MeCN has been shown by other workers to be an efficient quencher of thione  $S_2$  states *via* H-donation [30].

High quantum yields for RT phosphorescence ( $\Phi_P$ ) have been reported for **PT** and **BPT** in perfluoroalkane solvents, with  $\Phi_P=0.33$  and  $\Phi_P=0.08$  respectively for excitation into the  $S_2$  band [11, 12]. Due to the strong solvent interaction of both the  $S_2$  and  $T_1$  states of thione compounds, only perfluoroalkane solvents have been shown to be sufficiently inert to permit the study of intramolecular photo-physical processes of the larger thione compounds in



**Fig. 5** Cyclic voltammograms of (a) **PT** and (b) **BPT** in MeCN. The relative current of the **PT** wave is shifted by +30  $\mu A$  to allow comparison on the same diagram

**Table 3** Cyclic voltammetry data

Thione	$E_{1/2}/V^a, {}^b (E_{pa}-E_{pc}/mV)$	$E_p^{ox}/V$	$E_p^{red}/V$
1	–	+1.06	–0.06 –0.37
2	–	–	–1.36
3	–1.39 (80)	–	–
4	–1.00 (70)	–	–1.56
5	–1.00 (75) –1.54 (120) <sup>d</sup>	–	–1.56

<sup>a</sup> All given against SHE from a ferrocene internal standard,  $E_{1/2}(Fc/Fc^+) = 0.424$  V vs. SHE. All measurements carried out in MeCN.

<sup>b</sup>  $E_{1/2}$  is the measured half-wave potential for the reversible reduction process.  $E_{pa}-E_{pc}$  is a measure of the peak-to-peak separation determined from the peak potentials at the maximum current of the corresponding anodic ( $E_{pa}$ ) and cathodic ( $E_{pc}$ ) waves.

<sup>c</sup>  $E_p^{ox}$  and  $E_p^{red}$  are the measured peak potentials for the irreversible oxidation and reduction waves respectively.

<sup>d</sup> Quasi-reversible

solution [31]. The phosphorescence quantum yields obtained for **DMIT** and **DMIKT** for infinite dilution in PF-1,3,-DMCH following excitation into  $S_2$  were measured as  $\Phi_p=0.149$  ( $\pm 0.015$ ) and  $\Phi_p=0.018$  ( $\pm 0.002$ ) respectively (Table 2).  $\Phi_p$  was not determined for **DMIDT** due to its photoinstability.

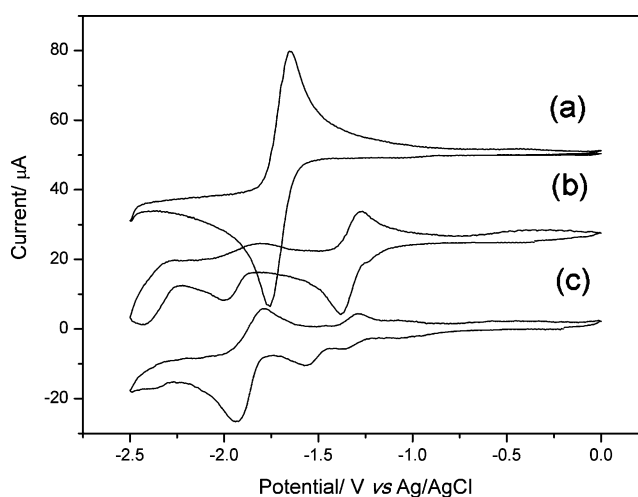
The high RT phosphorescence quantum yield observed for **PT** is attributed to the fact the  $T_1-S_0$  energy gap is relatively large in comparison to other thiones, which leads to a relatively small Franck–Condon factor for  $T_1 \rightarrow S_0$  intersystem crossing (ISC) [11]. A relatively high phosphorescence radiative rate constant ( $1.1 \times 10^4$  s<sup>-1</sup>) is also obtained for **PT** in PF-1,3,-DMCH [11]. In contrast, the  $T_1-S_0$  energy gap in **DMIT** and **DMIKT** is smaller, and as such the Franck–Condon factor for non-radiative decay of the  $T_1$  state to  $S_0$  by ISC is expected to be larger. Furthermore, the presence of methyl groups alpha to the C=S moiety have been shown to provide Franck–Condon factors which favour radiationless triplet decay in other aromatic thiones [11]. This may explain the much lower phosphorescence quantum yields obtained for **DMIT** and **DMIKT** and indeed **TMIT** as well. Attempts to synthesise thiones of similar structure to **DMIT**, **DMIKT** and **DMIDT** but without the  $\alpha$ -methyl groups proved unsuccessful and it is believed their presence is required to stabilise the C=S moiety.

The cyclic voltgrams of **PT** and **BPT** are shown in Fig. 5. Both compounds give a series of irreversible oxidation and reduction waves, for which the corresponding peak potentials,  $E_p^{ox}$  and  $E_p^{red}$ , are shown in Table 3. The reason for this irreversible oxidation process is unclear, but may potentially be due to electropolymerisation. The cyclic voltgrams of **DMIT**, **DMIKT** and **DMIDT** are shown in Fig. 6 and the corresponding peak

potentials are shown in Table 3. The redox behaviour of these thiones is complex. **DMIT** shows a single reversible one-electron reduction. In addition to a similar reversible reduction wave, **DMIKT** also shows two additional broad irreversible reduction peaks. **DMIDT** also shows the same strong reversible reduction wave, a broad irreversible reduction wave, and a second reduction with a half-wave potential,  $E_{1/2}=1.53$  V, which appears to be quasi-reversible. At a scan rate of 100 mV s<sup>-1</sup> and a temperature of 25 °C, peak-to-peak separations ( $E_{pa}-E_{pc}$ ) for the reversible reduction wave observed for thiones **DMIT**, **DMIKT** and **DMIDT** were between *ca.* 0.70 and 0.80 mV in MeCN. Whilst these values are slightly larger than the 59 mV expected for a reversible one-electron process, they are comparable with  $E_{pa}-E_{pc}$  obtained for the ferrocene–ferrocenium couple obtained under the same conditions. The ratios of the anodic and cathodic peak currents for this reversible reduction wave are close to unity and changing the scan rate has no effect on  $E_{pa}-E_{pc}$ . The quasi-reversible reduction wave observed for **DMIDT** was also detected at faster scan rates and  $E_{pa}-E_{pc}$  for this wave was *ca.* 120 mV. The large peak-to-peak separation obtained for this wave is consistent with a quasi-reversible process.

## Discussion

Prior to this study **PT** and **BPT** attracted our attention for OLED applications due to their high RT phosphorescence quantum yields ( $\Phi_p=0.47$  and 0.12 respectively for selective excitation into  $T_1$ ) [11, 12]. Although both compounds readily undergo vacuum sublimation, without any thermal degradation, the cyclic voltammetry studies shown here



**Fig. 6** Cyclic voltammograms of (a) **DMIT**, (b) **DMIKT** and (c) **DMIDT** in MeCN. The relative current of the **DMIT** and **DMIKT** waves are shifted by +50 and +25  $\mu$ A respectively to allow comparison on the same diagram

indicate irreversible redox chemistry, which is undesirable in OLED devices.

**DMIT**, **DMIKT** and **DMIDT** exhibit RT phosphorescence which extends into the near IR region. The  $\Phi_p$  values reported here for **DMIT** and **DMIKT** of  $\Phi_p=0.149$  and  $0.019$  respectively were obtained for excitation into the  $S_2$  level, and it is known that the phosphorescence quantum yield for direct excitation into  $T_1$  of **TMIT** is *ca.* twice that for excitation in  $S_2$ , ( $\Phi_p=0.068$  and  $\Phi_p=0.12$  for excitation into  $S_2$  and  $T_1$ , respectively [12]), presumably because of other non-radiative processes competing with ISC from  $S_2$  into the triplet manifold. We might then anticipate an emission yield somewhat greater than those reported here when the  $T_1$  state is populated directly, e.g. in OLED applications, where the method of excited state population is electrical- rather than photo-excitation. In such circumstances the low extinction coefficients for the  $S_0-T_1$  transition, for example  $\epsilon=4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$  for **TMIT** [10], are irrelevant and since, under electrical excitation, excitons are formed in both singlet and triplet states with a spin statistic ratio of 1:3, direct population of the  $T_1$  state would be expected to be efficient. Since,  $S_1-T_1$  intersystem crossing rate constants are frequently close to unity for thiones [8–9], this would also enable excited states formed by singlet excitons to be utilized. The reversible redox chemistry exhibited by **DMIT** also meets another of the requirements for OLED technology, although a triplet lifetime of  $40 \mu\text{s}$  is on the limits of suitability. The photophysical data reported here were obtained from solution phase studies; however in OLEDs triplet emitters are immobilised in a rigid polymer host layer. Since flexible molecular structures can provide channels for non-radiative deactivation [32], immobilization within a polymer host may minimise or even eliminate these pathways. Furthermore, a host matrix may help to improve the photostability of the thione triplet emitter. Thus, while the solution phase properties of the novel thiones reported here may not be optimum for commercial applications, further studies in polymer or solid-state matrices may still be worthwhile. Examination and understanding of the molecular and environmental factors that control the key photochemical and electrochemical characteristics of thiones and other main-group triplet emitters, such as: triplet energies, rates of radiative and non-radiative triplet deactivation, and reversibility of redox reactions, will undoubtedly help drive forward advances in the design of novel triplet emitters.

## Conclusions

The preparation and characterisation of two new far-red/near-infrared emitting thiones, **DMIKT** and **DMIDT**, has been described and their photophysical and electrochemistry compared to those of the known thiones, **PT**, **BPT**, and **DMIT**.

Addition of the additional carbonyl or thione group to give **DMIKT** and **DMIDT** shifts the emission maxima *ca.* 50 nm to the red of **DMIT**. There is also a significant reduction in triplet lifetime along this series from  $44 (\pm 2) \mu\text{s}$  (**DMIT**) to  $10 (\pm 0.8) \mu\text{s}$  (**DMIKT**) in PF-1,3-DMCH and  $8.6 (\pm 0.5) 1.3 (\pm 0.5)$  and  $0.35 (\pm 0.07) \mu\text{s}$  (**DMIDT**) in acetonitrile. There is also a reduction in the rate constant for ground-state quenching of the triplet, from  $9.8 (\pm 0.9)$  to  $3.5 (\pm 0.6)$  and  $1.3 (\pm 0.2) \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  for the same series of compounds in acetonitrile. While **DMIT** gives a relatively high phosphorescence yield of  $0.149 (\pm 0.015)$ , that for **DMIKT** is  $0.018 (0.002)$  and that for **DMIDT** has not been obtained because of its photo-instability. While **PT** and **BPT** exhibit irreversible redox behaviour, **DMIT**, **DMIKT** and **DMIDT** all show at least one reversible reduction wave, attributed to a one-electron process centred on the C=S moiety. **PT**, **BPT** and **DMIKY** were stable to vacuum sublimation. Attempts to synthesize thiones of similar structure to **DMIT**, **DMIKT** and **DMIDT** but without the  $\alpha$ -methyl groups proved unsuccessful and it is believed their presence may be required to stabilize the C=S moiety.

In terms of potential for application in OLEDs, phosphorescence quantum yields, triplet lifetimes, and redox reversibility are promising. There are issues with thermal and photostability, but further work in solid and polymer matrices is recommended before these difficulties are used to unequivocally dismiss thiones as practical triplet emitters for far-red/near-infrared OLEDs.

**Acknowledgements** RCE would like to acknowledge the University of Wales Swansea (UWS) for provision of a research studentship and Kodak European R&D for financial support. Thanks are extended to Dr Chris P. Morley at Cardiff University for use of the cyclic voltammetry equipment and for useful discussion. Mass spectra were recorded by the EPSRC National Mass Spectrometry Centre located at UWS. Mr Ian Matthews (UWS) is acknowledged for technical support (NMR).

## References

- Hung LS, Chen CH (2002) Recent progress of molecular organic electroluminescent materials and devices. *Mater Sci Eng Rep* 39 (5–6):143–222 doi:10.1016/S0927-796X(02)00093-1
- Geffroy B, le Roy P, Prat C (2006) Organic light-emitting diode (OLED) technology: materials, devices and display technologies. *Polym Int* 55(6):572–582 doi:10.1002/pi.1974
- Baldo MA, Thompson ME, Forrest SR (2000) High-efficiency fluorescent organic light-emitting devices using a phosphorescent sensitizer. *Nature* 403(6771):750–753 doi:10.1038/35001541
- Yersin H (2004) Triplet emitters for OLED applications. Mechanisms of exciton trapping and control of emission properties. *Top Curr Chem* 241:1–26
- Evans RC, Douglas P, Winscom CJ (2006) Coordination complexes exhibiting room-temperature phosphorescence: evaluation of their suitability as triplet emitters in organic light emitting diodes. *Coord Chem Rev* 250(15–16):2093–2126 doi:10.1016/j.ccr.2006.02.007



6. Kunkely H, Vogler A (2001) Luminescent metal complexes: diversity of excited states. *Top Curr Chem* 213:143–182
7. Bhattacharyya K, Das PK, Ramamurthy V, Rao VP (1986) Triplet-state photophysics and transient photochemistry of cyclic enethiones—a laser flash photolysis study. *J Chem Soc, Faraday Trans II* 82:135–147 doi:10.1039/f29868200135
8. Steer RP, Ramamurthy V (1988) Photophysics and intramolecular photochemistry of thiones in solution. *Acc Chem Res* 21(10):380–386 doi:10.1021/ar00154a005
9. Maciejewski A, Steer RP (1993) The photophysics, physical photochemistry, and related spectroscopy of thiocarbonyls. *Chem Rev* 93(1):67–98 doi:10.1021/cr00017a005
10. Maciejewski A, Szymanski M, Steer RP (1986) Thermally activated delayed S1 fluorescence of aromatic thiones. *J Phys Chem* 90(23):6314–6318 doi:10.1021/j100281a051
11. Szymanski M, Steer RP, Maciejewski A (1987) The phosphorescence of 4H-pyran-4-thione: Large quantum yields from room-temperature fluid solutions. *Chem Phys Lett* 135(3):243–248 doi:10.1016/0009-2614(87)85149-7
12. Maciejewski A, Szymanski M, Steer RP (1988) Photophysics and photochemistry of thione triplets in fluid solution. *J Phys Chem* 92(24):6939–6944 doi:10.1021/j100335a020
13. Sikorski M, Khemlinskii IV, Augustyniak W, Wilkinson F (1996) Triplet state decay of some thioketones in solution. *J Chem Soc, Faraday Trans* 92(19):3487–3490 doi:10.1039/f9969203487
14. Szymanski M, Maciejewski A, Steer RP (1988) Radiationless decay of aromatic thiones in solution selectively excited to their S3, S2, S1 and T1 states. *J Phys Chem* 92(9):2485–2489 doi:10.1021/j100320a019
15. Maciejewski A, Jakubowska A, Dutkiewicz E, Augustyniak W (1996) Spectral and photophysical properties of aromatic thiones in micellar systems: xanthione as convenient absorption and emission probes. *J Colloid Interface Sci* 177(2):528–541 doi:10.1006/jcis.1996.0067
16. Milewski M, Sikorski M, Maciejewski A, Mir M, Wilkinson F (1997) Primary photophysical properties of 4H-1-benzopyran-4-thione in cyclodextrin complexes. *J Chem Soc, Faraday Trans* 93(17):3029–3034 doi:10.1039/a702062g
17. Sikorski M, Wilkinson F, Steer RP (1998) Photophysics of aromatic thioketones supported on cellulose. *J Chem Soc, Faraday Trans* 94(13):1855–1859 doi:10.1039/a802424c
18. Becker RS, Chakravorti S, Gartner CA, Miguel MG (1993) Photosensitizers—comprehensive photophysics, photochemistry, and theory of coumarins, chromones, their homologs and thione analogs. *J Chem Soc, Faraday Trans* 89(7):1007–1009 doi:10.1039/f9938901007
19. Kunkely H, Vogler A (2008) Telluroxanthone: a new type of triplet emitter. *Inorg Chem Commun* 11(1):36–38 doi:10.1016/j.inoche.2007.10.010
20. Yeung LL, Yip YC, Luh T-Y (1990) Transition-metal promoted reactions: W(CO)6-mediated desulfurization of dithioketals—evidence for a thione intermediate. *J Org Chem* 55(6):1874–1881 doi:10.1021/jo00293a037
21. Nishio T, Okuda N, Kashima C (1996) Intramolecular [2+2] photocycloaddition of 2-allylindane-1-thiones. *Liebigs Ann* 1:117–120
22. Ranu BC, Jana U (1999) A new redundant rearrangement of aromatic ring fused cyclic alpha-hydroxydithiane derivatives. Synthesis of aromatic ring fused cyclic 1,2-diketones with one-carbon ring expansion. *J Org Chem* 64(17):6380–6386 doi:10.1021/jo990634s
23. Jeong I-L, Nagao Y (1999) Intermolecular tandem carbopalladation—carbocyclic one-atom ring-expansion reaction using hydroxy methoxyallenylindanones: novel synthesis of 4-oxo-alpha-tetraones. *Synlett* 5:576–578
24. Pederson BS, Scheibye S, Nilsson NH, Lawesson S-O (1978) Studies on organophosphorus compounds. 10. Synthesis of thioketones. *Bull Soc Chim Belg* 87(3):223–228
25. Scheibye S, Shabana R, Lawesson S-O, Romming C (1982) Studies on organo-phosphorus compounds: reactions of ketones with 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide. *Tetrahedron* 38(7):993 doi:10.1016/0040-4020(82)85078-3
26. Brown NMB, Bladon P (1965) Proton magnetic resonance spectra of 4-pyrone, 1-thia-4-pyrone, 4-thiopyrone and 1-thia-4-thiopyrone. *Spectrochim Acta [A]* 21(7):1277
27. Crosby GA, Demas JN (1971) Measurement of photoluminescence quantum yields—review. *J Phys Chem* 75(8):991 doi:10.1021/j100678a001
28. Lacowicz JR (1999) Principles of fluorescence spectroscopy 2nd Ed. Kluwer Academic/Plenum, New York
29. Seybold PG, Gouterman M (1969) Porphyrins. 13. Fluorescence spectra and quantum yields. *J Mol Spectrosc* 31(1):1 doi:10.1016/0022-2852(69)90335-X
30. Burdzinski G, Maciejewski A, Buntinx G, Poizat O, Lefumeux C (2004) Ultrafast quenching of the excited S-2 state of benzopyranthione by acetonitrile. *Chem Phys Lett* 384(4–6):332–338 doi:10.1016/j.cplett.2003.12.029
31. Maciejewski A (1990) The application of perfluoroalkanes as solvents in spectral, photophysical and photochemical studies. *J Photochem Photobiol A* 50(2):87–131 doi:10.1016/1010-6030(90)87046-E
32. Turro NJ (1991) Modern molecular photochemistry. University Science Books, New York