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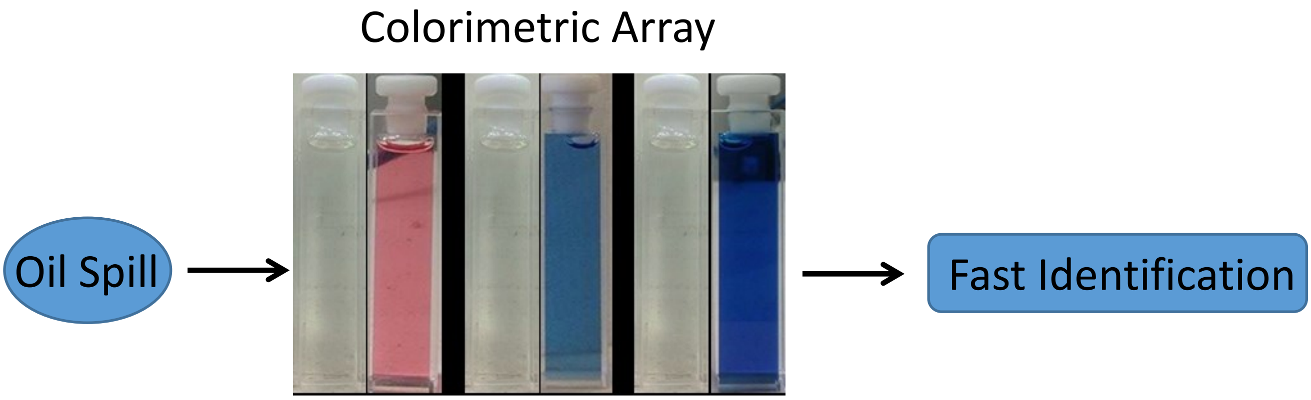
Graphical Abstract



Facile Oil Spill Source Identification using Colorimetric Detection

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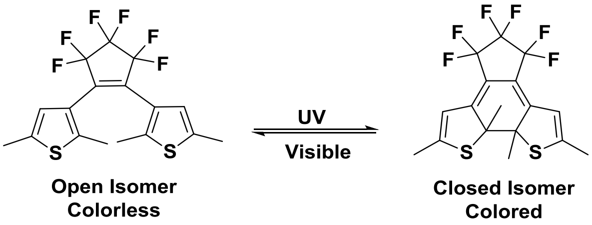
Abstract

The colorimetric detection of polycyclic aromatic hydrocarbons (PAHs) was investigated for the quick and easy identification of likely oil spill offenders. In this new technology, photochromic compounds were used to sense PAHs by varying their photoswitching capacity. To that end, three photochromes were designed and showed varying degrees of photoswitching inhibition depending on PAH analyte, photochrome and excitation wavelength. PAH mixtures that mimic oil spills showed the same varying response and demonstrated the accuracy of this technology. To prove the applicability of this technology, an array was assembled using the three photochromes at three excitation wavelengths and tested against authentic crude oil samples. Not only could these samples be differentiated, weathering of two distinctly different oil samples showed limited variation in response, demonstrating that this may be a viable technique for *in situ* oil identification.

Introduction

Oil spills in marine environments can have detrimental long-term effects on marine ecosystems.[1] With shipping (and other industries) under greater financial and timetable constraints, the number of worldwide illegal pollution events (both intentional and unreported accidents) is growing,[1] in particular, in crowded ports and harbours. For instance, since 2000 there have been more than 3000 oil pollution incident reports recorded in Australian waters - most of which have occurred in harbours.[1] Therefore, a quick, portable, robust and reliable oil screening and identification technology is needed to analyse and identify the source of the spill.

The current available analytical processes are cumbersome laboratory-based technologies, requiring extensive, expensive and time-consuming evidential quality sampling and analysis of all possible oily spaces (fuel, waste, cargo and oil tanks and pipes) in each vessel. One characteristic frequently used to discriminate oils is the relative composition of various polycyclic aromatic hydrocarbons (PAHs).[2] The relative amounts of PAHs can be determined through various chromatographic techniques, such as gas chromatography (GC).[3] Although highly effective, GC is not portable and requires hazardous hydrogen and expensive helium. Therefore, spectroscopic determination provides the opportunity to revolutionise this methodology especially as light sources and sensors are becoming smaller and more powerful.[3c, 4] Spectroscopic methods for identifying and quantifying PAHs have been developed and include fluorescence, absorption, infrared and raman spectroscopies.[2a, 3b, 3c, 4-5] To that end, we recently reported a new colorimetric method for the detection of individual and mixtures of PAHs using photochromic compounds.[6] Photochromic compounds are materials that reversibly switch between two isomeric forms through photoexcitation (Scheme 1), which present distinct optical properties (often colorless and colored).[7] In this technology, the degree of photoisomerisation varied according to the molar absorptivity of the PAHs present and the photochromic compound at a given excitation wavelength.[6] In general, the more the PAH absorbed the excitation light, the more it inhibited the photoisomersation reaction, and hence the difference in the color intensity. This is a powerful technique; the simple visible change in color could allow non-specialist operators to use this technology and to make a quick and accurate assessment of PAH content.



Scheme 1: Photoisomerisation of a photochromic compound undergoing ring closing and ring opening reactions.

In the present study, we explored the effect of the photochrome structure on the PAH sensing capability and developed an array that could further distinguish individual PAHs. To test its feasibility, this array technology was applied to four crude oil samples. Finally, we established the reliability of this technology to identify the oil type/source by analysing two weathered oil samples.

Results and discussion

The diarylethene (DAE) class of photochromic compounds used in this study have a unique combination of properties, including thermal stability, fatigue resistance, fast response, and high cyclization quantum yields.[7b, 8] Materials with these properties are routinely used in the optoelectronic industry for molecular switches, optical memory devices and chemical sensors.[7b, 9] In this study, three DAEs were designed to vary the extent of conjugation in order to expand the optical window of the array, where the conjugation length is DAE1 < DAE2 < DAE3 (Figure 1).

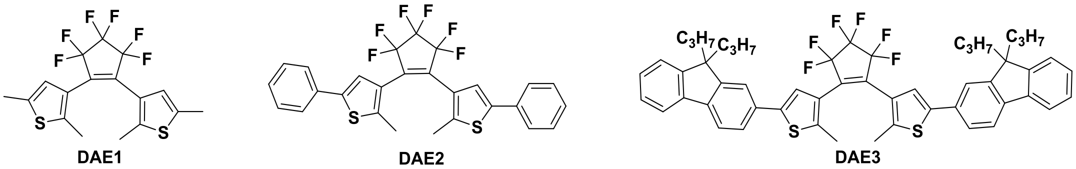


Figure 1: Diarylethene-type photochromic compounds used in this study.

Optical Characterisation:

The absorption spectra of the three photochromes in the ring opened and closed forms are depicted in Figure 2a. The three photochromic compounds are colorless in the open form (Figure 2b). The open form of DAE1 has a similar absorption spectrum as DAE2 while DAE3 revealed a red-shifted absorption spectrum. The photochromic compounds follow the same trend in the closed form. An important optical property for PAH sensing is the molar absorptivity (ε) of the DAE, which dictates how well the DAE absorbs light at a particular wavelength. Table 1 summarises the absorption characteristics of the three DAEs and their corresponding molar absorptivities at particular wavelengths. DAE1 has a low molar absorptivity at all three wavelengths. DAE2 on the other hand has a low molar absorptivity at 325 nm but a high molar absorptivity at both 275 nm and 295 nm. Conversely, DAE3 has a very high molar absorptivity at 325 nm and lower molar absorptivity at 275 and 295 nm, although still higher than DAE1. Therefore, this series of photochromic compounds span the UV-range where PAHs absorb.

The photoconversion quantum yield (from ring opened to closed) dictates the number of excited molecules that convert from the open to the closed form; the larger the quantum yield of photoconversion the higher the probability that the PAH will affect the photoconversion process. That is, if the quantum yield of photoconversion is unity, then every photon absorbed by the opened DAE will convert to the closed DAE. The presence of a light-absorbing PAH may therefore have a most pronounced effect on this photoconversion process, as compared to a DAE with a low photoconversion. In this series of photochromes, the quantum yield at 313 nm excitation of DAE1 is 0.40, DAE2 is 0.59 and DAE3 is 0.91.[10] The high photoconversion of DAE3 is likely due to the extended stabilisation that occurs through the extended conjugation imparted by the fluorenyl moieties.

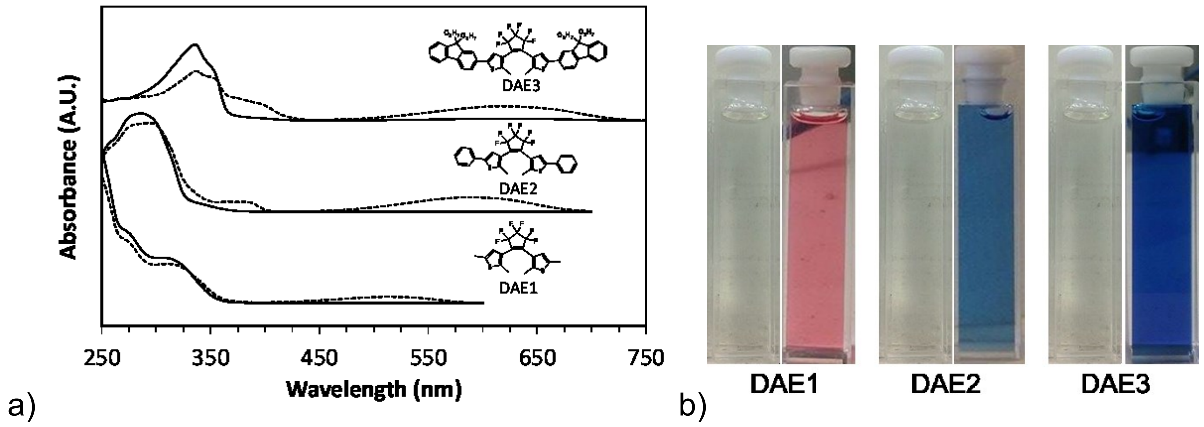


Figure 2: a) Absorption profile of diarylethenes DAE1, DAE2 and DAE3 in both ring opened (solid) and closed isomeric forms (dashed). b) Color change for each DAE before (left) and after (right) excitation.

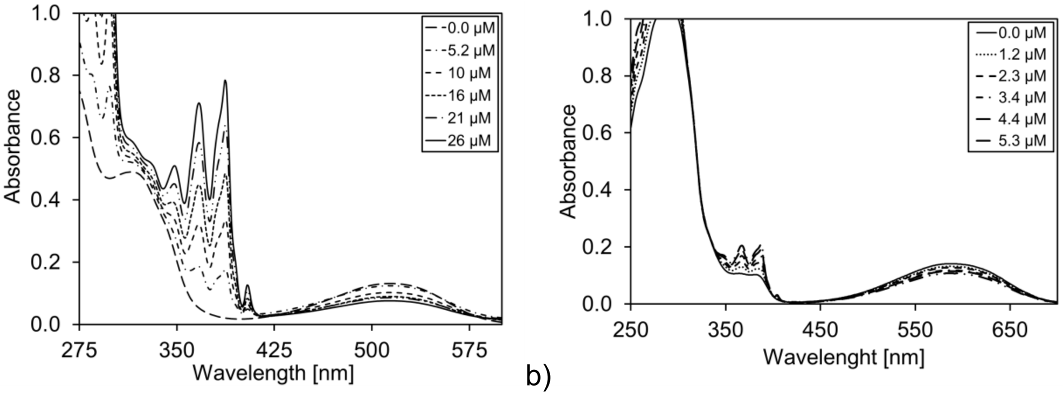
Table 1: Summary of the molar absorptivity (ε) at 275, 295 and 325 nm and the relative quantum yield (Φ) of photoconversion from opened to closed forms of the three diarylethenes (DAEs) in this study.

Photochrome	ε_{275} ($M^{-1}cm^{-1}$)	ε_{295} ($M^{-1}cm^{-1}$)	ε_{325} ($M^{-1}cm^{-1}$)	$\Phi_{o\rightarrow c}$ (@ 313 nm)	$\Phi_{o\rightarrow c}$ (@ 275 nm)
DAE1	7,700	5,100	4,000	0.40[11b]	0.10
DAE2	36,650	36,650	7,000	0.59[10]	0.59
DAE3	21,700	29, 600	61,600	0.91	0.70

Sensing individual PAHs:

The photoswitching inhibition of DAE1, DAE2 and DAE3 was performed using chrysene, pyrene, benzo(*a*)pyrene, phenanthrene, naphthalene and toluene. Figure 3 depicts the absorption spectra due to photoisomerization of the three DAEs as a function of the benzo(*a*)pyrene concentration. The degree of photoswitching inhibition can be represented by a linear relationship between the PAH concentration and the change of the closed-form photochrome absorbance, Equation 1. This relationship is analogous to the Stern-Volmer fluorescence quenching (Figure 3d), where A_o and A are the absorption intensity in the absence and presence of analyte (PAH), respectively, K_{psv} is the *pseudo* Stern-Volmer constant and [PAH] is the analyte concentration.[12]

$$\frac{A_0}{A} = 1 + K_{psv}[PAH] \qquad (1)$$



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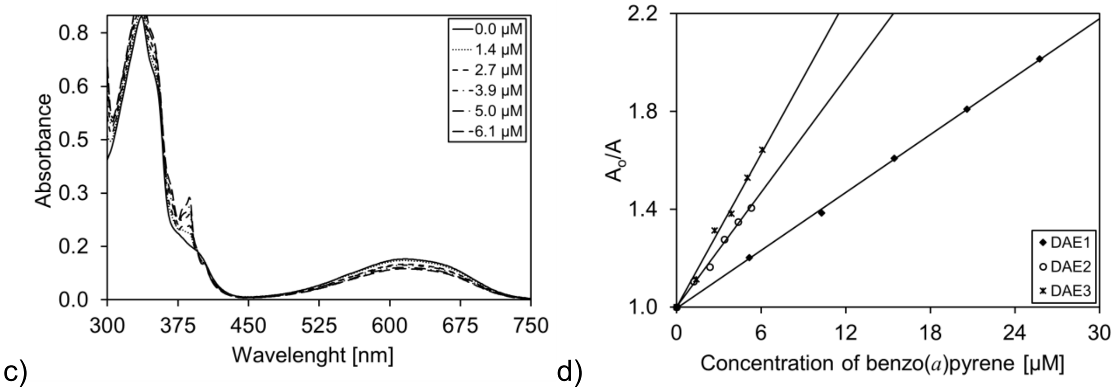

Figure 3: Absorption spectra of diarylethene (DAE) solutions as a function of benzo(*a*)pyrene concentration after exposing each sample at 275 nm: (a) DAE1, (b) DAE2 and (c) DAE3. (d) Photoswitching inhibition (ratio of the integrated absorbance) of the three DAEs as a function of benzo(*a*)pyrene concentration.

Table 2 summarises the K_{psv}s of the various DAEs with the corresponding discrete PAH when excited at 275 nm. For DAE3, the trend in the analyte sensitivity is toluene < naphthalene < phenanthrene < benzo(*a*)pyrene < pyrene < chrysene, which follows exactly the molar absorptivity of the PAH at 275 nm. This trend indicates that the analyte molar absorptivity directly correlates to the photoswitching inhibition, where the analyte attenuates the number of exciting photons for photoisomerisation. DAE1 and DAE2 behave similarly except in the presence of pyrene, a response attributed to the sharpness of the analyte absorption at the excitation wavelength.[6]

The effect of the excitation wavelength on the photoswitching inhibition of DAE3 using phenanthrene as the analyte is depicted in Figure 4a. The photoswitching inhibition was greatest at 275 nm excitation and lowest at 325 nm. This excitation wavelength dependency on the photoswitching inhibition correlates well with the optical density of the analyte at the excitation wavelength. Figure 4a illustrates the absorption spectrum of phenanthrene as compared to the photostationary state of the three DAEs. The analyte absorbs well at 275 and 295 nm, while the absorption at 325 nm is negligible. Therefore, the more the analyte absorbs at the excitation wavelength, the higher the photoswitching inhibition, which is consistent with the above analyte molar absorptivity and photoswitching inhibition trend. These DAEs in combination have the potential to provide selectivity for differentiating PAH fingerprints.[6]

Table 2: Molar absorptivity coefficient (ε) of the various PAHs compared to their respective *pseudo* Stern-Volmer constant (K_{psv}) values at 275 nm excitation wavelength using diarylethenes DAE1, DAE2 and DAE3.

Analyte	ε_{275nm} ($M^{-1}cm^{-1}$)	K_{psv} (M^{-1})		
		DAE1	DAE2	DAE3
Toluene	89[a]	530 ± 100	2,550 ± 110	1,680 ± 110
Naphthalene	38,000	7,280 ± 660	15,750 ± 1,380	15,330 ± 890
Phenanthrene	30,200	19,530 ± 1,000	79,050 ± 5,870	69,130 ± 4,940
Benzo(*a*)pyrene	13,600	39,530 ± 730	82,720 ± 7,100	106,790 ± 4,200
Pyrene	43,100	23,150 ± 1,370	60,240 ± 5,400	139,500 ± 4,560
Chrysene	4,300	50,100 ± 1,270	228,210 ± 15,700	184,040 ± 6,280

[a] Value taken from ref. [13]

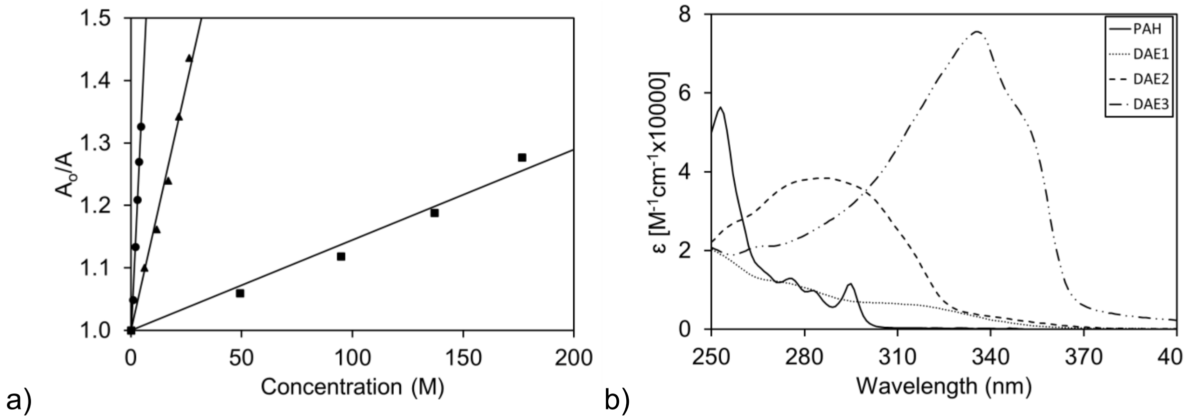

Figure 4: a) Photoswitching inhibition of diarylethene DAE3 as a function of phenanthrene concentration at 275 nm (●) and 295 nm (▲) and 325 nm (■). b) Molar absorptivity coefficient of phenanthrene (PAH) compared to the three different photochromic compounds.

The effect of the DAE structure on the photoswitching inhibition was analysed. The PAH sensitivity follows the general trend: DAE1 < DAE2 ≈ DAE3 (Figure 5), likely due to the quantum yield of photoconversion from the open to the closed state at the excitation wavelength. At 275 nm, DAE1 has the lowest photoconversion efficiency, hence the lowest K_{psv}. DAE2 and DAE3 have a similar photoconversion efficiency at 275 nm (Table 1), and therefore their K_{psv} values are similar. Hence, the response of the photoswitching for a particular PAH can vary based on the DAE and the excitation wavelength used. This property may be helpful in further differentiating PAH fingerprints in oil spills.

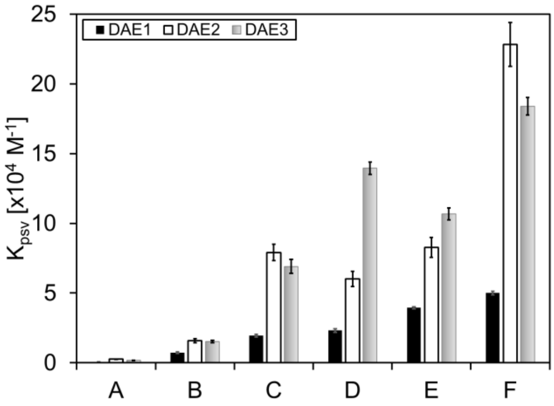

Figure 5: Comparison of the K_{psv} constants of toluene (A), naphthalene (B), phenanthrene (C), benzo(*a*)pyrene (D), pyrene (E) and chrysene (F) at 275 nm excitation for the three diarylethenes (DAE) tested.

Oil Spill Mimics:

Four oil spill mimics were created by simply mixing various compositions of phenanthrene, naphthalene and chrysene, thereby generating unique known PAH fingerprints. As for individual PAHs, the colorimetric analysis of these mixtures was performed in the presence of DAE1, DAE2 and DAE3 (Table 3). The K_{psv} of each mixture was predicted by multiplying the K_{PSV}s of the analytes by the mole ratio. Comparison of the theoretical K_{PSV}s with the experimental K_{PSV}s provided a means by which the accuracy of the response could be determined (Table 3). The theoretical and experimental results were similar, indicating this technology can reliably differentiate unique combinations of PAHs, as is present in oil samples.

Table 3: Comparison between the predicted and experimental *pseudo* Stern-Volmer constant (K_{PSV}) for each of the PAH mixtures tested and their respective photochromic compound at 275 nm excitation.

Photochrome	Mixture	Phenanthrene [%]	Naphthalene [%]	Chrysene [%]	Predicted K_{PSV} (M^{-1})	Experimental K_{PSV} (M^{-1})
DAE1	1	26.6	55.7	17.7	18,120 ± 510	16,810 ± 1,620
DAE1	2	4.4	92.6	3.0	9,080 ± 620	7,310 ± 780
DAE1	3	78.4	16.4	5.2	19,120 ± 780	14,040 ± 1,160
DAE1	4	10.3	21.5	68.2	37,770 ± 890	43,000 ± 5,060
DAE2	1	23.3	59.9	16.8	66,220 ± 3090	65,360 ± 2,140
DAE2	2	8.3	85.7	6.0	33,800 ± 1590	45,140 ± 3,660
DAE2	3	15.5	39.8	44.7	120,530 ± 7100	91,440 ± 4,390
DAE2	4	54.9	35.2	9.9	71,500 ± 3610	83420 ± 5700
DAE3	1	11.4	80.7	7.8	34,700 ± 1040	37,700 ± 2,800
DAE3	2	8.2	58.1	33.7	76,650 ± 2220	72,760 ± 3,520
DAE3	3	43.7	51.3	5.0	47,220 ± 2230	60,460 ± 4,830
DAE3	4	2.3	96.2	1.5	19,170 ± 870	19,720 ± 1170

Oil spill assessment:

To determine the efficacy of this technology, the response of four different crude oil samples (Tapis Crude, Bahrain Crude, Widuri Crude and Bass Strait Crude) was analysed. The photoswitching inhibition experiment was repeated using these oils to determine the colorimetric response as a function of the excitation wavelength and DAE to generate a 3 x 3 array (Table 4). Each of the four oil samples exhibited a unique response according to the excitation wavelength and DAE (similar to that of the individual PAHs). The 3 x 3 array is necessary because the selectivity would be limited without it. For instance, Bass Strait Crude and the Bahrain Crude would have the same output if DAE1 was only used at three excitation wavelengths. DAE2 and DAE3 respond differently at those wavelengths (driven by the quantum yield of photoconversion), whereby providing a unique colorimetric response for both Bass Strait Crude and the Bahrain Crude. This colorimetric array is therefore a fast, easy and cheap method to identify oils, and when combined with pattern recognition software could be particularly powerful.[14]

Table 4: Summary of the *pseudo* Stern-Volmer constants ($K_{PSV,}$ $mg^{-1}.10$ mL) of four oil samples analysed using the 3 x 3 colorimetric detection methodology.

Oil	DAE	K_{PSV} @275 nm	K_{PSV} @295 nm	K_{PSV} @325 nm
Tapis Crude	1	160.31 ± 16.52	158.27 ± 10.53	78.59 ± 6.64
	2	114.32 ± 9.89	69.15 ± 11.38	30.89 ± 4.02
	3	110.09 ± 7.95	93.12 ± 9.74	25.44 ± 1.10
Bahrain Crude	1	469.99 ± 13.57	377.03 ± 47.69	260.07 ± 33.96
	2	376.21 ± 22.40	164.34 ± 13.92	131.64 ± 10.75
	3	326.03 ± 29.64	231.07 ± 14.37	79.33 ± 9.93
Widuri Crude	1	212.56 ± 3.35	220.86 ± 5.89	190.41 ± 22.59
	2	192.74 ± 12.39	166.98 ± 8.30	147.33 ± 18.89
	3	177.29 ± 19.32	128.27 ± 19.19	58.07 ± 7.81
Bass Strait Crude	1	405.24 ± 27.65	366.37 ± 29.02	315.27 ± 39.65
	2	174.96 ±74.96	158.95 ± 20.46	111.58 ± 25.38
	3	121.37 ± 24.44	81.47 ± 12.01	24.28 ± 3.36

Conclusions:

The potential of three diarylethene photochromic compounds towards the development of a quick and simple methodology for identifying oil spill offenders was investigated. The commercially available diarylethenes DAE1 and DAE2 were compared with DAE3, designed with greater conjugation, to further understand the effect of the photochrome characteristics on the PAH sensing behaviour. DAE2 and DAE3 showed the highest sensitivity while DAE1 showed the lowest. This difference was rationalised by the different quantum yield of photoconversion. Oil spill mimics established the accuracy of this technology; the observed photoswitching inhibition was similar to that of the predicted values. Furthermore, the technique was found to be applicable to, and able to readily differentiate between, authentic oil samples. Based on this systematic study, this technology represents a simple approach to the quick identification of oils and as such is highly amenable to *in situ* applications.

Experimental

Materials

The commercially available PAHs (Sigma-Aldrich) were used as received and solutions prepared in freshly distilled dichloromethane (DCM - Univar). The preparation of compound 1, 2, DAE1 and DAE2 were prepared according to literature methods.[10-11] DAE3 was prepared using direct arylation of 3-bromo-2-methylthiophene,[15] followed by metal-halogen exchange,[16] as described in the Supporting Information. The crude oil samples Tapis Crude (Malaysian), Bahrain Crude (Bahrain), Widuri Crude (Indonesian) and Bass Strait Crude (Australian) were provided by the Australian Institute of Marine Science (AIMS) and used as received.

Characterization

Absorption spectra were recorded using a Shimadzu UV1800 or a Cary 5E UV-Vis-NIR spectrophotometer. A PerkinElmer LS-50B luminescence spectrometer was used as a source of light for photoswitching the photochomic solutions. All experiments were performed in 1 cm quartz cuvettes. The relative quantum yields of photoconversion were performed as previously described at 313 nm.[10-11] The quantum yields at 275 nm were estimated using DAE2 = 0.59 as a reference.

Three photochrome DCM solutions (0.100 mM DAE1, 0.030 mM DAE2 and 0.011 mM DAE3) were used as stock solutions to prepare the PAH solutions in order to maintain a constant photochrome concentration. The *pseudo* Stern-Volmer constants were calculated by comparing the integrated absorption area (400 to 600 nm of DAE1, 400 to 700 nm of DAE2 and 425 to 750 nm of DAE3) and dividing by the total volume of the solution, with the coefficients and errors reported based on an average of five measurements.

Four oil solutions prepared in 10 mL DCM (2.200 mg for Tapis Crude, 1.600 mg for Bahrain Crude, 1.900 mg for Widuri and 1.500 mg for Bass Strait Crude) were prepared and diluted. The *pseudo* Stern-Volmer constants of the oils were calculated as per the analyte solutions described above. The coefficients and errors were based on an average of five measurements, and the constants obtained in mg^{-1}.10 mL units.

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