

# Simple 1-dicyanomethylene-2-chloro-3-aminoindene push–pull chromophores: applications in cation and anion sensing†

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Push–pull chromophores based on 1-dicyanomethylene-2-chloro-3-aminoindene are readily synthesized. These compounds undergo dramatic colour changes in the presence of metal cations as a result of the interaction of the amino substituent with the analytes. One of these compounds is a selective copper(II) colorimetric probe in acetonitrile solution, displaying a dramatic colour change upon coordination of the amine group to the metal centre. These compounds are also selective cyanide sensors in acetonitrile solution because of the disruption of the intramolecular charge transfer process as the result of the nucleophilic addition of the anion to the indene moiety.

## Introduction

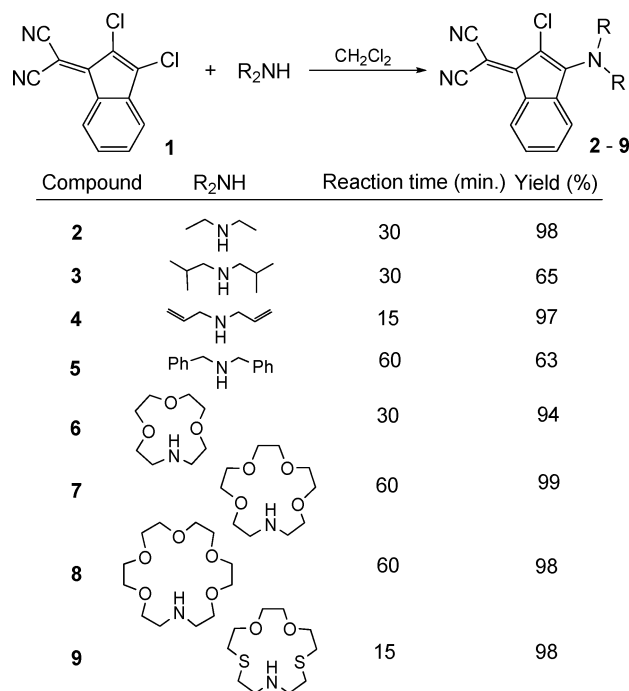
Development of molecular probes capable of detecting cations, anions or neutral molecules by a change in their optical signals is an area of intense research.<sup>1</sup> Industrial processes often demand detection methods that require sophisticated instrumentation such as atomic absorption/emission spectrometry or inductively coupled plasma mass spectrometry.<sup>2</sup> These analytical techniques are not very suitable for fast detection protocols. Therefore, it is important to develop methods allowing rapid, straightforward analyte detection. In this regard, colorimetric sensors offer the advantage of providing information with minimal equipment, allowing the so-called “naked-eye” detection. There are numerous examples of colorimetric probes for anionic and cationic species.<sup>3</sup> Common drawbacks of these systems are that they often require complicated synthesis and their design is not flexible, therefore every analyte requires its own probe design.

In this work we describe an easy entry to a family of push–pull chromophores based on 3-amino-1-dicyanomethyleneindene moieties. These compounds are readily obtained by amination reactions and they proved to be useful sensors for the detection of cationic and anionic species. In a previous communication, we have used this strategy to decorate a mesoporous solid with this type of signalling unit, giving rise to a sensor of primary amines.<sup>4</sup>

## Results and discussion

### Synthesis and characterization of novel compounds

Reaction of 1-dicyanomethylene-2,3-dichloroindene<sup>5</sup> **1** with different secondary amines in dichloromethane at room temperature gave the 1-dicyanomethylene-2-chloro-3-aminoindene chromophores **2–9** in good yields (Scheme 1). Nucleophilic substitution of the chlorine atom in position 3 is selective and the reaction occurred with a wide range of amines. The presence of donor amino and acceptor dicyanomethylene groups in these molecules resulted in an intramolecular charge transfer band responsible for their intense deep purple colour. Thus the UV/vis spectra of these compounds showed an intense band centred around



Scheme 1 Synthesis of compounds **2–9**.

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† Electronic supplementary information (ESI) available: NMR spectra of **2–10**, UV-vis, <sup>1</sup>H NMR and MS titration experiments. CCDC reference numbers 744017. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b916700e

550 nm. Compounds **2–9** were obtained as deep purple solids and spectroscopically characterized. The structure of compound **3** was further confirmed by X-ray diffraction. Two different views of the structure are shown in Fig. 1. The structural features of the molecule showed the conjugation of the dicyanomethylene and the diethylamine groups of the chromophore. Thus, the dicyanomethylene indene moiety is coplanar with the aromatic system and the nitrogen atom showed  $sp^2$  hybridization with angles around the amine nitrogen atom close to  $120^\circ$ . The bond distance between this atom and the indene carbon is  $1.343 \text{ \AA}$  and the dihedral angle of the amine and the pseudoaromatic system is  $40.3^\circ$ .

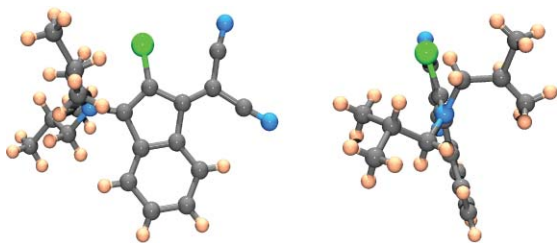


Fig. 1 Two different views of the crystal structure of compound **3**.

### Cation sensing

Since the strong colour displayed by compounds **2–9** is the result of an intramolecular charge transfer band from the amine to the dicyanomethyleneindene moieties we reasoned that coordination of the amine to a metal centre would impact the conjugation of the molecule resulting in a change of colour.

We first investigated the diethylamino derivative **2**. Addition of 1 equivalent of different cations added as their triflate or perchlorate salts to a  $10^{-4} \text{ M}$  solution of **2** in acetonitrile resulted in a change of colour in the presence of  $\text{Sc}^{3+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Al}^{3+}$ , and especially  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  (Fig. 2 top).

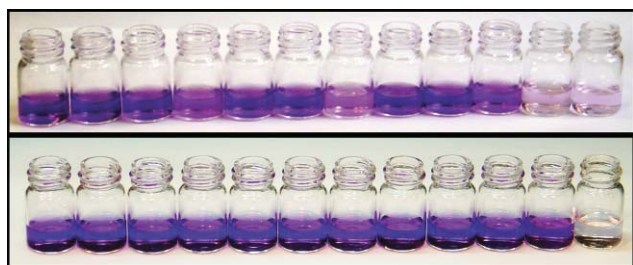


Fig. 2 Colour changes of receptors **2** (top row) and **4** (bottom row) ( $10^{-4} \text{ M}$  in acetonitrile) upon addition of 1 equiv. of different cations. From left to right: none,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ .

The UV/vis spectrum of this compound showed an intense band with a maximum at  $\lambda = 550 \text{ nm}$  ( $\epsilon = 10\,324 \text{ M}^{-1} \text{ cm}^{-1}$ ). Addition of increasing amounts of these cations resulted in the quenching of this band accounting for the bleaching observed in the presence of some of the cations (Fig. 3). An isosbestic point appeared at approximately  $343 \text{ nm}$  and the changes of the absorbance at  $550 \text{ nm}$  fitted to a  $1:1$  model. Apparent association constants are included in Table 1.

Table 1 Association constants ( $\log K_a$ ) for receptors **2**, **4** and **9** with different cations (added as their triflate or perchlorate salts) at  $298 \text{ K}$  in MeCN as determined by UV-vis titration techniques

	2	4	9
$\text{Al}^{3+}$	$4.47 \pm 0.03$	—	—
$\text{Cu}^{2+}$	$5.17 \pm 0.06$	$5.93 \pm 0.23$	$5.70 \pm 0.08$
$\text{Fe}^{3+}$	$5.56 \pm 0.09$	—	—
$\text{Hg}^{2+}$	—	—	$3.67 \pm 0.14^a$
			$6.36 \pm 0.18^a$
$\text{Sc}^{3+}$	$3.96 \pm 0.67$	—	—
$\text{Sn}^{2+}$	$4.54 \pm 0.11$	—	—

<sup>a</sup> The titration profile fits a sequential  $1:1:1:1$  complexation process.

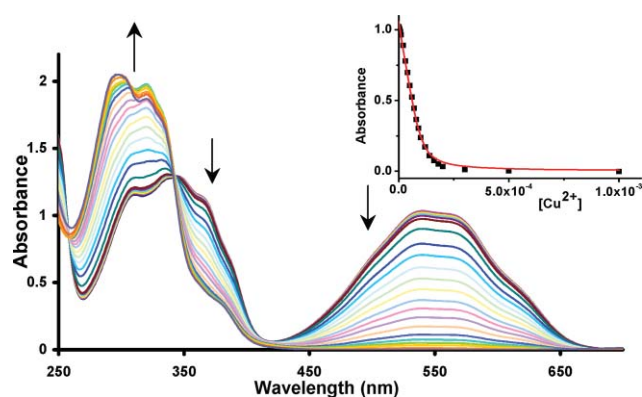
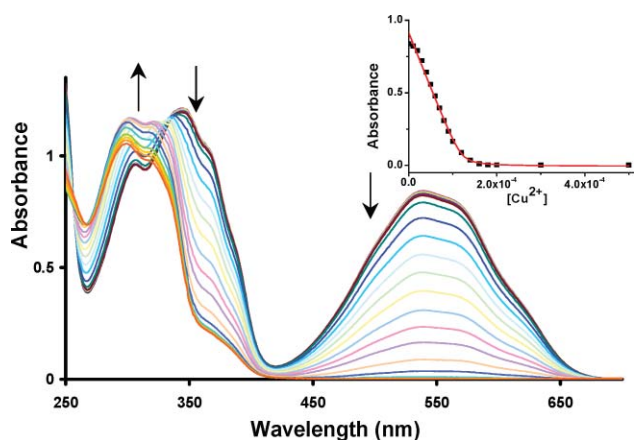


Fig. 3 UV-vis spectral changes of receptor **2** ( $10^{-4} \text{ M}$ ) upon addition of increasing amounts of  $\text{Cu}^{2+}$  ( $0 \rightarrow 10$  equiv.) in acetonitrile. Inset: titration profile of the observed changes at  $\lambda = 550 \text{ nm}$ .

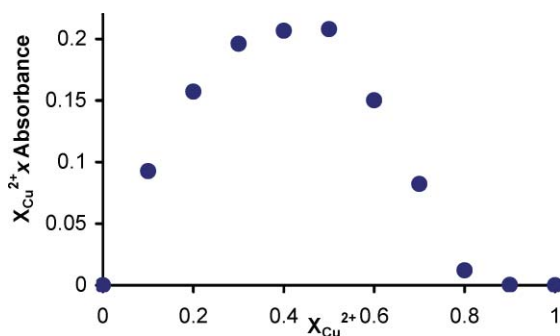
From all these experiments it is clear that compound **2** is able to interact with different cations, signalling this event by a dramatic change of colour. The lack of selectivity showed by this compound can be explained in terms of the simplicity of the binding unit. Therefore, the presence of more elaborate binding units with additional coordination sites could improve the selectivity of the probe. We next investigated the response of compound **4**, bearing two allyl groups, towards the same set of cations in acetonitrile solution, as it was expected that the allyl groups could participate in the coordination of the metal (Fig. 2 bottom). In this case, a selective bleaching of the solution was observed only in the presence of  $\text{Cu}^{2+}$  (perchlorate salt). Similar changes in the UV/vis spectra to those described for compound **2** were observed, with disappearance of the band centred at  $539 \text{ nm}$  upon addition of the metal (Fig. 4).

An isosbestic point appeared at approximately  $255 \text{ nm}$  and the changes of the absorbance at  $539 \text{ nm}$  fitted to a  $1:1$  model. Association constants are shown in Table 1. Job's plot analysis of the UV-Vis titration of **4** and  $\text{Cu}^{2+}$ , carried out in MeCN, revealed a maximum at a 50% mole fraction, in accordance with the proposed  $1:1$  binding stoichiometry (Fig. 5). The detection limit of **4** ( $10^{-4} \text{ M}$  in MeCN), calculated by the blank variability method,<sup>6</sup> was  $9.46 \times 10^{-8} \text{ M}$ .

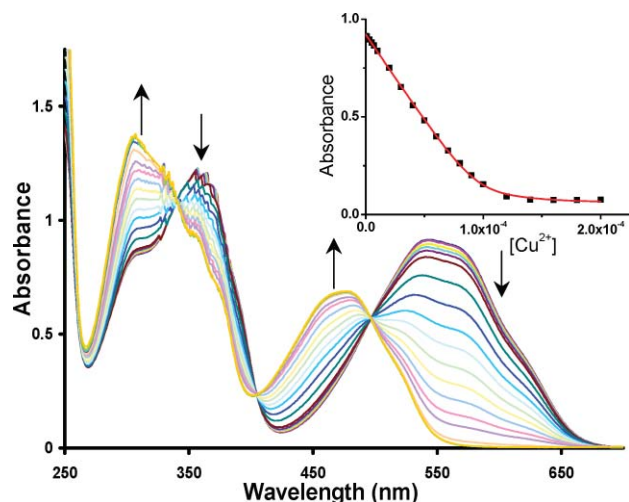
We then studied the macrocyclic derivatives **6–9**. Compounds **6–7** did not show immediate colour changes in the presence of the usual cations, showing partial decolourisation after 20 min in the presence of  $\text{Sc}^{3+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  and compound **8** showed only partial decolourisation in the presence of  $\text{Pb}^{2+}$ .



**Fig. 4** UV-vis absorption spectrophotometric titration of compound **4** ( $10^{-4}$  M) with increasing amounts of  $\text{Cu}^{2+}$  (0  $\rightarrow$  5 equiv.) in acetonitrile. Inset: variation of absorbance at  $\lambda = 539$  nm vs. concentration of metal.



**Fig. 5** Job's plot analysis of **4** ( $10^{-4}$  M in MeCN) with  $\text{Cu}^{2+}$ .

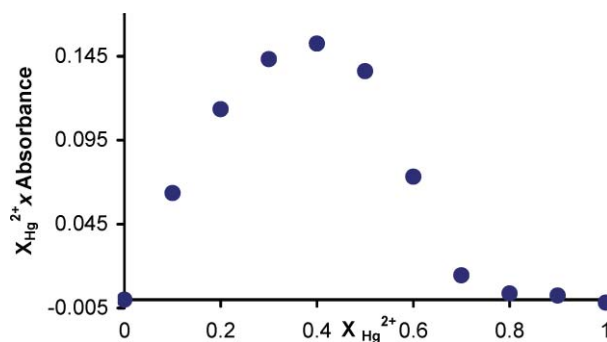


**Fig. 6** UV-vis absorption spectrophotometric titration of compound **9** ( $10^{-4}$  M) with increasing amounts of  $\text{Cu}^{2+}$  (0  $\rightarrow$  2 equiv.) in acetonitrile. Inset: variation of absorbance at  $\lambda = 550$  nm vs. concentration of metal cation.

and  $\text{Fe}^{3+}$ . Instead compound **9** underwent colour changes in the presence of  $\text{Hg}^{2+}$  (decolourisation) and  $\text{Cu}^{2+}$  (purple to yellow).† A UV/vis titration experiment with increasing amounts of copper(II) perchlorate is shown in Fig. 6. Decreasing of the band centred at  $\lambda = 550$  nm and appearance of a new band at 478 nm was observed, with isosbestic points at 498 and 343 nm. These changes fitted a

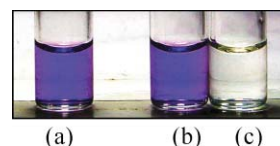
1 : 1 ML binding model with  $\log K_a = 5.70 \pm 0.08$  (Table 1). In the case of  $\text{Hg}^{2+}$  the changes in the UV-vis were best described as a sequential 1 : 1 + 1 : 1 process with  $\log K_{a1} = 3.67 \pm 0.14$  and  $\log K_{a2} = 6.36 \pm 0.18$  (Table 1).

Job's plot analysis of the UV-Vis titration of **9** and  $\text{Cu}^{2+}$ , carried out in MeCN, also revealed a maximum at a 50% mole fraction, thus confirming the 1 : 1 binding mode (see ESI†). But the Job's plot analysis of the UV-Vis titration of **9** and  $\text{Hg}^{2+}$ , carried out in MeCN, revealed a maximum at a 40% mole fraction, confirming in this case the proposed 2 : 1 binding stoichiometry (Fig. 7).



**Fig. 7** Job's plot analysis of **9** ( $10^{-4}$  M in MeCN) with  $\text{Hg}^{2+}$ .

The sensing action of **4** and  $\text{Cu}^{2+}$  was equally effective in a mixture of a  $10^{-4}$  M solution of **5** and 2 equiv. of every cation:  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Ag}^{+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  in MeCN, without losing sensitivity to  $\text{Cu}^{2+}$  (Fig. 8).



**Fig. 8** (a) A solution of **4** ( $10^{-4}$  M in MeCN). (b) Addition of 2 equiv. of every cation:  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Ag}^{+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  to solution (a). (c) Addition of 2 equiv. of  $\text{Cu}^{2+}$  to solution (b).

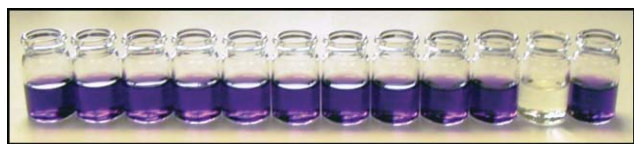
In addition, a  $10^{-4}$  M solution of **4** that lost the colour in the presence of 4 equiv. of  $\text{Cu}^{2+}$  ( $\text{ClO}_4^-$ )<sub>2</sub>, recovered the colour in the presence of 2 equiv. of 3,6-dioxa-1,8-octanedithiole, thus proving the reversibility of the detection (see ESI†).

### Anion sensing

Cyanide is one of the most toxic anions yet is widely used industrially.<sup>7</sup> Therefore, development of cyanide receptors and sensors is an area of interest.<sup>8</sup> Among the various strategies used to produce these probes, those relying on the nucleophilicity of this anion have proven successful.<sup>9</sup> Since our system could undergo nucleophilic additions we decided to explore the interactions of the diethylamino derivative **2** with anions. Addition of 10 equivalents of different anions added as their tetrabutylammonium salts to a  $10^{-4}$  M solution of **2** in acetonitrile resulted in a selective bleaching of the solution in the presence of  $\text{CN}^-$  (Fig. 9). The same behaviour was observed for the rest of compounds **3–9**.

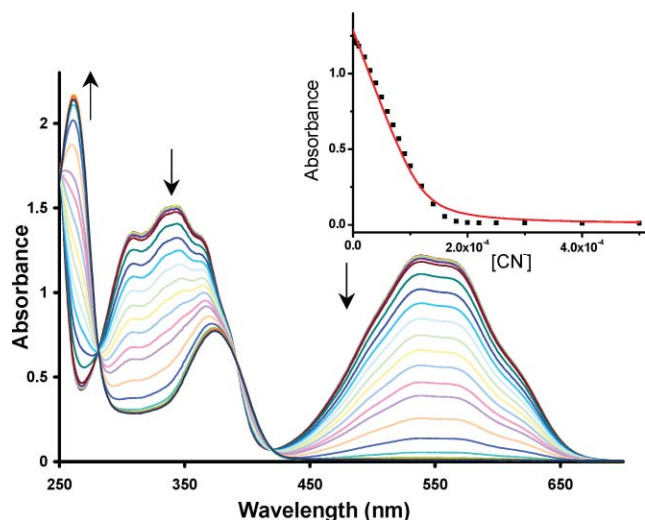
UV-Vis spectra reflected these changes with the disappearance of the absorbance in the 550 nm region and appearance of isosbestic points at *ca.* 390, 291 and 252 nm for compound **2**





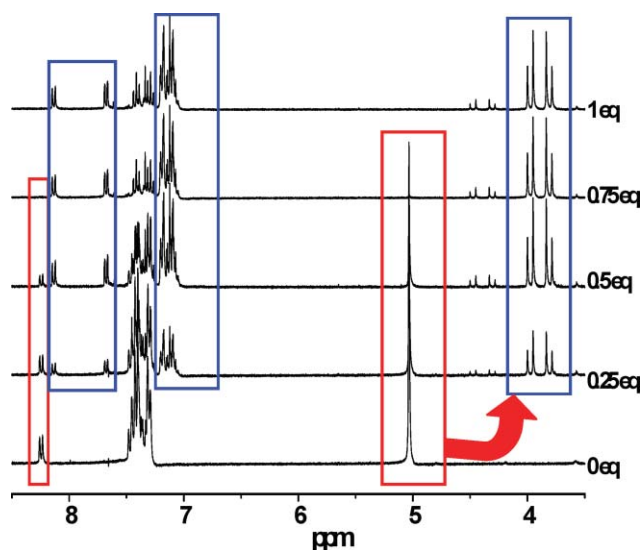
**Fig. 9** Colour changes induced by the addition of 10 equiv. of different anions to a solution of receptor **2** ( $10^{-4}$  M in acetonitrile). From left to right: none,  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $BzO^-$ ,  $NO_3^-$ ,  $H_2PO_4^-$ ,  $HSO_4^-$ ,  $AcO^-$ ,  $CN^-$ ,  $SCN^-$ .

(Fig. 10). The changes in the absorbance as a function of the concentration of anion added can be fitted to a 1:1 binding equilibrium model, giving an association constant of  $\log K_a = 6.39 \pm 0.28$ . The detection limit of **2** ( $10^{-4}$  M in MeCN), calculated by the blank variability method,<sup>6</sup> was  $1.01 \times 10^{-7}$  M.

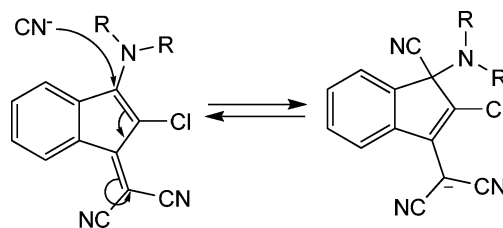


**Fig. 10** UV-vis spectral changes of receptor **2** ( $10^{-4}$  M) upon addition of increasing amounts of TBACN (0  $\rightarrow$  5 equiv.) in acetonitrile. Inset: titration profile of the observed changes at  $\lambda = 550$  nm.

In order to shed light on the interaction of cyanide and receptor **2**, NMR titration experiments were carried out.  $^1H$  NMR titration of **2** with 1 equiv.  $CN^- Bu_4N^+$  in  $CDCl_3$  causes a large upfield shift of the methylene group signals, from  $\delta$  3.9 to 2.7, that become diastereotopic (two sextets), indicating a close proximity to a quaternary chiral centre.  $^{13}C$  NMR (and DEPT) titration of **2** and  $CN^-$  (1 equiv) show an adduct (see ESI<sup>†</sup>) having two equivalent CN groups (a double intensity signal at  $\delta$  126), a third CN group at  $\delta$  111, and two new quaternary carbon signals at  $\delta$  72 and 26, all of them corresponding most probably to the addition product shown in Scheme 2.<sup>†</sup> The NMR changes by titration with cyanide are even clearer by using the dibenzylamine derivative **5**, which undergoes similar colorimetric changes upon addition of cyanide. This process is slow on the NMR time scale (Fig. 11). Addition of cyanide resulted in the disappearance of the signals corresponding to the receptor and the appearance of a new set of signals. The biggest difference corresponded to the methylene protons of the amine substituents which underwent an upfield shift of approximately 1.2 ppm whereas only minor changes are observed for the aromatic protons. All these data suggest a nucleophilic attack at the carbon 3 as the likely mechanism for the interaction between **2** and cyanide (Scheme 2). Nucleophilic addition of



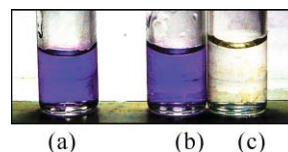
**Fig. 11**  $^1H$  NMR (300 MHz) titration of chromophore **5** (13 mM) with  $CN^-$  in  $CD_3CN$ . In red: signals disappearing. In blue: signals appearing during titration.



**Scheme 2** Proposed mechanism for the addition of cyanide to the indene moiety.

cyanide anion to the indene ring would induce the formation of a stereogenic carbon, therefore the methylene protons would become diastereotopic and hence the signal pattern observed. This mechanism is also supported by the fact that the parent 3-amino-1-dicyanomethyleneindene compound **10**, lacking the chlorine atom in the 2 position, showed no changes in the presence of cyanide. This result could be explained because of the attenuated electrophilicity of the chromophore as the result of the lack of the electron-withdrawing halogen atom.

The sensing action of **2** and  $CN^-$  was equally effective in a mixture of a  $10^{-4}$  M solution of **2** and 2 equiv. of every anion:  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $BzO^-$ ,  $NO_3^-$ ,  $H_2PO_4^-$ ,  $HSO_4^-$ ,  $AcO^-$  and  $SCN^-$  in MeCN, without losing sensitivity to  $CN^-$  (Fig. 12).



**Fig. 12** (a) A solution of **2** ( $10^{-4}$  M in MeCN). (b) Addition of 2 equiv. of every anion:  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $BzO^-$ ,  $NO_3^-$ ,  $H_2PO_4^-$ ,  $HSO_4^-$ ,  $AcO^-$  and  $SCN^-$  to solution (a). (c) Addition of 2 equiv. of  $CN^-$  to solution (b).

A  $10^{-4}$  M solution of **2** that lost the colour in the presence of 4 equiv. of  $CN^- Bu_4N^+$ , recovered the colour in the presence of 4 equiv. of  $Ag^+ ClO_4^-$ . The low resolution EIMS spectrum of a

mixture of **4** and 1 equiv.  $\text{CN}^-$  showed only the peaks characteristic of **4**. Both experiments proved the reversibility of the detection (see ESI<sup>†</sup>).

## Conclusions

Amination of 1-dicyanomethylene-2,3-dichloroindene provides straightforward access to a family of push–pull chromophores. One of these compounds is a selective copper(II) colorimetric probe in acetonitrile solution, displaying a dramatic colour change upon coordination of the amine group to the metal centre. The selectivity of the probe for  $\text{Cu}^{2+}$  depends on the basicity of the amine nitrogen and the interaction of the lateral groups. It is improved by the presence of the diallylamine group but is worse when dialkylamine or azacrown ether groups are present. Those compounds are also selective cyanide dosimeters under similar conditions, through the nucleophilic addition of the anion to the indene moiety. The simplicity and versatility of the design could offer opportunities for improved designs. Efforts to develop fluorochromogenic probes based on this fragment are currently under way in our laboratory.

## Experimental

### Materials and instrumentation

The reactions performed with air sensitive reagents were conducted under dry nitrogen. The solvents were previously distilled under nitrogen over calcium hydride or sodium filaments. Commercial reagents were used as received. 1-Dicyano-2,3-dichloroindene was synthesized as previously reported.<sup>2</sup> Melting points were determined in a Gallenkamp apparatus and are not corrected. Infrared spectra were registered in a Nicolet Impact 410 spectrometer in potassium bromide tablets. NMR spectra were recorded in Varian Mercury-300 and Varian Unity Inova-400 machines, in  $\text{DMSO}-d_6$ ,  $\text{CDCl}_3$ ,  $\text{CD}_3\text{CN}$ ,  $\text{CD}_3\text{OD}$ . Chemical shifts are reported in ppm with respect to residual solvent protons, coupling constants ( $J_{\text{X-X'}}$ ) are reported in Hz. Elemental analyses of C, H and N were taken in a Leco CHNS-932. Mass spectra were taken in a Micromass AutoSpec machine, by electronic impact at 70 eV. Quantitative UV-visible measurements were performed with a Varian, Cary 300 Bio UV spectrophotometer, in 1 cm UV cells at 25 °C.

### Syntheses and characterization

**1-Dicyanomethylene-2-chloro-3-(*N,N*-diethylamino)indene (2).** Diethylamine (0.25 mL,  $\rho = 0.707 \text{ g mL}^{-1}$ , 2.421 mmol) was added to a solution of **1** (50 mg, 0.202 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL) at room temperature and the mixture stirred for 30 min. Then the reaction mixture was poured into a chilled solution of HCl in water (50 mL HCl, 10% w/v, and 100 g ice). The aqueous phase was extracted with dichloromethane ( $3 \times 30 \text{ mL}$ ). The combined organic extracts were dried ( $\text{Na}_2\text{SO}_4$ ) and the solvent evaporated. The residue was purified by flash chromatography (silica gel,  $1.5 \times 30 \text{ cm}$ ), from hexane– $\text{CH}_2\text{Cl}_2$  7 : 3 to 1 : 1, obtaining compound **2** as a purple solid. Yield 56 mg (98%). Mp 150–151 °C. **IR** (KBr,  $\text{cm}^{-1}$ ): 2202 (CN), 1600, 1588, 1511, 1483, 1476, 1452. **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 8.18 (d,  $J = 7.4 \text{ Hz}$ , 1H, CH=), 7.39 (d,  $J = 7.3 \text{ Hz}$ , 1H, CH), 7.31 (m, 2H, CH), 3.91 (c,  $J = 7.2 \text{ Hz}$ , 4H,  $\text{CH}_2$ ), 1.44

(t,  $J = 7.2 \text{ Hz}$ , 6H,  $\text{CH}_3$ ) ppm. **<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 157.33, 157.22, 134.96, 134.30, 131.06, 130.53, 123.46, 122.72, 116.97 (CN), 115.41 (CN), 99.05, 62.45, 46.95 ( $\text{CH}_2$ ), 14.63 ( $\text{CH}_3$ ) ppm. **MS (EI)**  $m/z$  (%): 285 ( $\text{M}^+ + 2$ , 35), 284 ( $\text{M}^+ + 1$ , 19), 283 ( $\text{M}^{++}$ , 100), 268 ( $\text{M}^+ - \text{CH}_3$ , 66), 248 ( $\text{M}^+ - \text{Cl}$ , 92), 240 (58), 227 (85), 220 (50), 177 (49), 176 (47). **HRMS**: Calc. for  $\text{C}_{16}\text{H}_{14}\text{N}_3\text{Cl}$ : 283.0876, found: 283.0864. **UV-Vis** ( $2.5 \times 10^{-5} \text{ M}$ ,  $\text{CH}_3\text{CN}$ ),  $\lambda$ : 538 nm ( $\epsilon = 9845 \text{ M}^{-1} \text{ cm}^{-1}$ ), 337 nm ( $\epsilon = 12071 \text{ M}^{-1} \text{ cm}^{-1}$ ), 237 nm ( $\epsilon_{\text{max}} = 15490 \text{ M}^{-1} \text{ cm}^{-1}$ ).

**1-Dicyanomethylene-2-chloro-3-(*N,N*-diisobutylamino)indene (3).** The procedure was similar to that described above using a solution of **1** (27 mg, 0.109 mmol) in 5 mL of  $\text{CH}_2\text{Cl}_2$  and diisobutylamine (0.25 mL,  $\rho = 0.740 \text{ g mL}^{-1}$ , 1.43 mmol) at room temperature and the mixture was stirred for 30 min. Chromatographic work up of the reaction crude (silica gel,  $1.5 \times 25 \text{ cm}$ , elution with hexane– $\text{CH}_2\text{Cl}_2$  6 : 4) yielded **3** as a purple solid. Yield 24 mg (65%). Mp: 163–164 °C. **IR** (KBr,  $\text{cm}^{-1}$ ): 2955, 2924, 2202 (CN), 1515, 1441, 1091. **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 8.25 (m, 1H, CH=), 7.35 (m, 3H, CH=), 3.58 (d,  $J = 7.5 \text{ Hz}$ , 4H,  $\text{CH}_2$ ), 2.06 (m, 2H, CH), 0.91 (d,  $J = 6.7 \text{ Hz}$ , 12H,  $\text{CH}_3$ ) ppm. **<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 157.88, 135.48, 134.21, 131.20, 130.06, 123.61, 122.24, 116.08 (CN), 114.49 (CN), 102.88, 65.26, 60.43 ( $\text{CH}_2\text{N}$ ), 27.72 (CH), 19.75 ( $\text{CH}_3$ ) ppm. **MS (EI)**  $m/z$  (%): 341 ( $\text{M}^+ + 2$ , 32), 340 ( $\text{M}^+ + 1$ , 26), 339 ( $\text{M}^{++}$ , 87), 304 ( $\text{M}^+ - \text{Cl}$ , 15), 296 (54), 283 (27), 240 (100), 177 (12). **HRMS**: Calc. for  $\text{C}_{20}\text{H}_{22}\text{N}_3\text{Cl}$ : 339.1502, found: 339.1487. **Crystal data** for **3**,  $\text{C}_{20}\text{H}_{22}\text{ClN}_3$ ,  $M = 339.86$ , triclinic,  $P\bar{1}$ ,  $a = 8.3304(16) \text{ \AA}$ ,  $b = 9.1897(18) \text{ \AA}$ ,  $c = 13.096(3) \text{ \AA}$ ,  $\alpha = 92.955(4)^\circ$ ,  $\beta = 97.382(4)^\circ$ ,  $\gamma = 108.536(4)^\circ$ ;  $V = 938.1(3) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.203 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 0.209 \text{ mm}^{-1}$ . Purple-black prism,  $(0.31 \times 0.13 \times 0.09) \text{ mm}^3$ . 4227 measured reflections, 2673 independent ( $R_{\text{int}} = 0.0248$ ), 1797 observed ( $I > 2\sigma(I)$ ).  $R_1 = 0.0873$ ,  $wR_2 = 0.1890$  (all data).<sup>†</sup>

**1-Dicyanomethylene-2-chloro-3-(*N,N*-diallylamino)indene (4).** The procedure was similar to that described above using a solution of **1** (30 mg, 0.122 mmol) in 5 mL of  $\text{CH}_2\text{Cl}_2$  and diallylamine (0.1 mL,  $\rho = 0.787 \text{ g mL}^{-1}$ , 0.811 mmol) at room temperature and the mixture was stirred for 15 min. Chromatographic work up of the reaction crude (silica gel,  $3 \times 20 \text{ cm}$ , elution with hexane– $\text{CH}_2\text{Cl}_2$  7 : 3) gave **4** as a purple solid. Yield 36 mg (97%). Mp: 117–118 °C. **IR** (KBr,  $\text{cm}^{-1}$ ): 2924, 2205 (CN), 1522, 1448, 1417, 1336, 1293. **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 8.19 (m, 1H, CH=), 7.41 (m, 1H, CH=), 7.30 (m, 2H, CH=), 5.98 (m, 2H, CH=), 5.44 (d,  $J = 10.4 \text{ Hz}$ , 2H,  $\frac{1}{2}\text{CH}_2$ =), 5.33 (d,  $J = 17.2 \text{ Hz}$ , 2H,  $\frac{1}{2}\text{CH}_2$ =), 4.38 (d,  $J = 5.2 \text{ Hz}$ , 4H,  $\text{CH}_2\text{N}$ ) ppm. **<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 157.75, 157.42, 134.31, 134.16, 131.98 (CH), 131.16 (CH), 130.35 (CH), 123.43 (CH), 122.63 (CH), 120.13 ( $\text{CH}_2$ =), 116.29 (CN), 114.68 (CN), 102.18, 99.67, 64.15, 53.53 ( $\text{CH}_2\text{N}$ ) ppm. **MS (EI)**  $m/z$  (%): 309 ( $\text{M}^+ + 2$ , 8), 307 ( $\text{M}^{++}$ , 22), 272 ( $\text{M}^+ - \text{Cl}$ , 100), 230 (44), 176 (19). **HRMS**: Calc. for  $\text{C}_{18}\text{H}_{14}\text{N}_3\text{Cl}$ : 307.0876, found: 307.0854. **UV-Vis** ( $10^{-4} \text{ M}$ ,  $\text{CH}_3\text{CN}$ )  $\lambda$ : 539 nm ( $\epsilon = 9139 \text{ M}^{-1} \text{ cm}^{-1}$ ), 342 nm ( $\epsilon = 13078 \text{ M}^{-1} \text{ cm}^{-1}$ ), 237 nm ( $\epsilon_{\text{max}} = 18363 \text{ M}^{-1} \text{ cm}^{-1}$ ).

**1-Dicyanomethylene-2-chloro-3-(*N,N*-dibenzylamino)indene (5).** The procedure was similar to that described above using a solution of **1** (30 mg, 0.121 mmol) in 10 mL of  $\text{CH}_2\text{Cl}_2$  and dibenzylamine (0.50 mL,  $\rho = 1.026 \text{ g mL}^{-1}$ , 2.604 mmol) at room temperature and the mixture was stirred for 60 min. Chromatographic work up

of the reaction crude (silica gel,  $3 \times 25$  cm, elution with hexane– $\text{CH}_2\text{Cl}_2$  4 : 6) yielded **5** as a purple solid. Yield 31 mg (63%). Mp: 178–179 °C. **IR** (KBr,  $\text{cm}^{-1}$ ): 3021, 2916, 2850, 2214 (CN), 1604, 1522, 1441, 1355.  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 8.30 (d,  $J$  = 8 Hz, 1H, CH=), 7.33 (m, 9H, CH=), 7.19 (m, 4H, CH=), 4.92 (s, 4H,  $\text{CH}_2\text{N}$ ) ppm.  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 158.60, 157.79, 135.16, 134.91, 134.01, 131.40, 130.35, 129.09, 128.23, 127.35, 123.81, 122.43, 115.96 (CN), 114.29 (CN), 101.65, 66.11, 54.81 ( $\text{CH}_2\text{N}$ ) ppm. **MS (FAB $^+$ )**  $m/z$  (%): 410 ( $\text{M}^+ + 3$ , 10), 409 ( $(\text{M}^+ + 2, 7)$ , 408 ( $\text{M}^+ + 1$ , 23), 407 ( $\text{M}^{++}$ , 11), 372 ( $\text{M}^+ - \text{Cl}$ , 3), 309 (11), 278 (14), 263 (10), 231 (43), 197 (10), 154 (71), 139 (12), 137 (100), 109 (30), 105 (12). **HRMS**: Calc. for  $\text{C}_{26}\text{H}_{18}\text{ClN}_3$ : 407.1189, found: 407.1196. **UV-Vis** ( $2.5 \times 10^{-5}$  M,  $\text{CH}_2\text{Cl}_2$ ),  $\lambda$ : 535 nm ( $\epsilon$  = 9666  $\text{M}^{-1} \text{cm}^{-1}$ ), 347 nm ( $\epsilon$  = 15 134  $\text{M}^{-1} \text{cm}^{-1}$ ), 301 nm ( $\epsilon$  = 10 112  $\text{M}^{-1} \text{cm}^{-1}$ ), 237 nm ( $\epsilon_{\text{max}}$  = 18 699  $\text{M}^{-1} \text{cm}^{-1}$ ).

**1-Dicyanomethylene-2-chloro-3-(4,7,10-trioxa-1-azacyclododec-1-yl)indene (6).** The procedure was similar to that described above using a solution of **1** (40 mg, 0.162 mmol) in 15 mL of  $\text{CH}_2\text{Cl}_2$  and 1,4,7-trioxa-10-azacyclododecane (70 mg, 0.400 mmol) at room temperature and the mixture was stirred for 30 min. Chromatographic work up of the reaction crude (silica gel,  $1.5 \times 30$  cm, elution with  $\text{CH}_2\text{Cl}_2$  to  $\text{CH}_2\text{Cl}_2$ –AcOEt 3 : 1) yielded **6** as a purple solid. Yield 58 mg (94%). Mp: 141–142 °C. **IR** (KBr,  $\text{cm}^{-1}$ ): 2928, 2858, 2202 (CN), 2189 (CN), 1599, 1525, 1479, 1444, 1157, 1090.  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 8.25 (m, 1H, CH=), 7.77 (m, 1H, CH=), 7.31 (m, 2H, CH=), 4.18 (t,  $J$  = 4.9 Hz, 4H,  $\text{CH}_2$ ), 3.96 (t,  $J$  = 4.9 Hz, 4H,  $\text{CH}_2$ ), 3.66 (m, 8H,  $\text{CH}_2$ ) ppm.  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 157.59, 157.02, 134.54, 134.29, 131.14, 130.21, 123.55, 123.32, 116.48 (CN), 114.90 (CN), 99.64, 70.99 ( $\text{CH}_2$ ), 70.93 ( $\text{CH}_2$ ), 70.02 ( $\text{CH}_2$ ), 53.35 ( $\text{CH}_2$ ) ppm. **MS (EI)**  $m/z$  (%): 387 ( $\text{M}^+ + 2$ , 14), 386 ( $\text{M}^+ + 1$ , 12), 385 ( $\text{M}^{++}$ , 40), 350 ( $\text{M} - \text{Cl}$ , 11), 298 (12), 262 (35), 248 (29), 239 (100), 225 (24), 190 (8), 176 (22). **HRMS**: Calc. for  $\text{C}_{20}\text{H}_{20}\text{N}_3\text{ClO}_3$ : 385.1193, found: 385.1182. **UV-Vis** ( $2.5 \times 10^{-5}$  M,  $\text{CH}_3\text{CN}$ ),  $\lambda$ : 533 nm ( $\epsilon$  = 10 861  $\text{M}^{-1} \text{cm}^{-1}$ ), 345 nm ( $\epsilon$  = 15 053  $\text{M}^{-1} \text{cm}^{-1}$ ), 233 nm ( $\epsilon_{\text{max}}$  = 21 285  $\text{M}^{-1} \text{cm}^{-1}$ ).

**1-Dicyanomethylene-2-chloro-3-(4,7,10,13-tetraoxa-1-azacyclopentadec-1-yl)indene (7).** The procedure was similar to that described above using a solution of **1** (40 mg, 0.162 mmol) in 20 mL of  $\text{CH}_2\text{Cl}_2$  and 1,4,7,10-tetraoxa-13-azacyclopentadecane (88 mg, 0.402 mmol) at room temperature and the mixture was stirred for 60 min. Chromatographic work up of the reaction crude (silica gel,  $1.5 \times 25$  cm, elution with  $\text{CH}_2\text{Cl}_2$  to AcOEt) yielded **7** as a purple solid. Yield 69 mg (99%). Mp: 193–194 °C. **IR** (KBr,  $\text{cm}^{-1}$ ): 2889, 2865, 2206 (CN), 2193, 1509, 1471, 1441, 1343, 1126.  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 8.25 (m, 1H, CH=), 7.53 (m, 1H, CH=), 7.32 (m, 2H, CH=), 4.13 (t,  $J$  = 6.0 Hz, 4H,  $\text{CH}_2$ ), 3.93 (t,  $J$  = 6.0 Hz, 4H,  $\text{CH}_2$ ), 3.65 (m, 12H,  $\text{CH}_2$ ) ppm.  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 157.36, 157.19, 134.45, 134.40, 131.19, 130.25, 123.38, 123.12, 116.50 (CN), 114.93 (CN), 99.41, 71.08 ( $\text{CH}_2$ ), 70.52 ( $\text{CH}_2$ ), 70.05 ( $\text{CH}_2$ ), 69.79 ( $\text{CH}_2$ ), 63.12, 54.46 ( $\text{CH}_2$ ) ppm. **MS (EI)**  $m/z$  (%): 429 ( $\text{M}^{++}$ , 2), 254 (39), 240 (56), 239 (100), 238 (75), 225 (36), 211 (12), 176 (16). **HRMS**: Calc. for  $\text{C}_{22}\text{H}_{24}\text{N}_3\text{ClO}_4$ : 429.1455, found: 429.1453. **UV-Vis** ( $2.5 \times 10^{-5}$  M,  $\text{CH}_3\text{CN}$ ),  $\lambda$ : 538 nm ( $\epsilon$  = 8303  $\text{M}^{-1} \text{cm}^{-1}$ ), 345 nm ( $\epsilon$  = 11 355  $\text{M}^{-1} \text{cm}^{-1}$ ), 302 nm ( $\epsilon$  = 8723  $\text{M}^{-1} \text{cm}^{-1}$ ), 234 nm ( $\epsilon_{\text{max}}$  = 16 532  $\text{M}^{-1} \text{cm}^{-1}$ ).

**1-Dicyanomethylene-2-chloro-3-(4,7,10,13,16-pentaoxa-1-azacyclooctadec-1-yl)indene (8).** The procedure was similar to that described above using a solution of **1** (30 mg, 0.121 mmol) in 10 mL of  $\text{CH}_2\text{Cl}_2$  and 1,4,7,10,13-pentaoxa-16-azacyclooctadecane (79 mg, 0.303 mmol) at room temperature and the mixture was stirred for 60 min. Chromatographic work up of the reaction crude (silica gel,  $1.5 \times 30$  cm, elution with  $\text{CH}_2\text{Cl}_2$  to AcOEt, then AcOEt–MeOH 3 : 1) yielded **8** as a purple solid. Yield 52 mg (90%). Mp: 84–85 °C. **IR** (KBr,  $\text{cm}^{-1}$ ): 2908, 2870, 2206 (CN), 1600, 1584, 1515, 1445, 1336, 1126.  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 8.23 (m, 1H, CH=), 7.55 (m, 1H, CH=), 7.30 (m, 2H, CH=), 4.19 (t,  $J$  = 5.3 Hz, 4H,  $\text{CH}_2$ ), 3.91 (t,  $J$  = 5.3 Hz, 4H,  $\text{CH}_2$ ), 3.65 (m, 16H,  $\text{CH}_2$ ) ppm.  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 158.36, 157.76, 134.86, 134.61, 131.42, 130.47, 123.60, 123.50, 116.76 (CN), 115.19 (CN), 100.31, 96.95, 70.92 ( $\text{CH}_2$ ), 70.85 ( $\text{CH}_2$ ), 70.78 ( $\text{CH}_2$ ), 70.36 ( $\text{CH}_2$ ), 53.27 ( $\text{CH}_2$ ) ppm. **MS (EI)**  $m/z$  (%): 475 ( $\text{M}^+ + 2$ , 9), 473 ( $\text{M}^{++}$ , 24), 438 ( $\text{M} - \text{Cl}$ , 16), 298 (44), 262 (38), 254 (41), 239 (100), 225 (35), 211 (20), 204 (26), 176 (24). **HRMS**: Calc. for  $\text{C}_{24}\text{H}_{28}\text{ClN}_3\text{O}_5$ : 473.1717, found: 473.1710. **UV-Vis** ( $2.5 \times 10^{-5}$  M,  $\text{CH}_3\text{CN}$ ),  $\lambda$ : 538 nm ( $\epsilon$  = 10 023  $\text{M}^{-1} \text{cm}^{-1}$ ), 348 nm ( $\epsilon$  = 13 377  $\text{M}^{-1} \text{cm}^{-1}$ ), 233 nm ( $\epsilon_{\text{max}}$  = 18 624  $\text{M}^{-1} \text{cm}^{-1}$ ).

**1-Dicyanomethylene-2-chloro-3-(1-aza-7,10-dioxo-4,13-dithia-cyclopentadecyl)indene (9).** The procedure was similar to that described above using a solution of **1** (40 mg, 0.16 mmol) in 20 mL of  $\text{CH}_2\text{Cl}_2$  and 10-aza-1,4-dioxo-7,13-dithiacyclopentadecane<sup>10</sup> (122 mg, 0.49 mmol, in 15 mL of  $\text{CH}_2\text{Cl}_2$ ) at room temperature and the mixture was stirred for 15 min. Chromatographic work up of the reaction crude (silica gel,  $3 \times 20$  cm, elution with  $\text{CH}_2\text{Cl}_2$  to ethyl acetate– $\text{CH}_2\text{Cl}_2$  1 : 5) yielded **9** as a purple solid. Yield 79 mg (98%). Mp: 194–196 °C. **IR** (KBr,  $\text{cm}^{-1}$ ): 2961, 2923, 2855, 2205 (CN), 1514, 1456, 1446, 1350, 1100.  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 8.27 (m, 1H, CH=), 7.36–7.32 (m, 3H, CH=), 4.14 (m, 4H,  $\text{CH}_2\text{N}$ ), 3.81 (m, 4H,  $\text{CH}_2\text{O}$ ), 3.66 (m, 4H,  $\text{CH}_2\text{O}$ ), 3.06 (m, 4H,  $\text{CH}_2\text{S}$ ), 2.76 (m, 4H,  $\text{CH}_2\text{S}$ ) ppm.  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 157.23, 156.34, 134.36, 134.33, 131.34, 130.30, 123.57, 122.56, 116.38 (CN), 114.77 (CN), 99.99, 77.20, 74.43 ( $\text{CH}_2\text{O}$ ), 70.55 ( $\text{CH}_2\text{O}$ ), 64.36, 53.92 ( $\text{CH}_2\text{N}$ ), 31.66 ( $\text{CH}_2\text{S}$ ), 31.56 ( $\text{CH}_2\text{S}$ ) ppm. **MS (IE)**  $m/z$  (%): 461 ( $\text{M}^{++}$ , 1), 426 ( $\text{M}^+ - \text{Cl}$ , 29), 360 (17), 301 (14), 242 (24), 211 (16), 184 (23), 142 (71), 123 (16), 103 (26), 87 (31), 75 (26), 60 (100). **HRMS**: Calc. for  $\text{C}_{22}\text{H}_{24}\text{N}_3\text{O}_2\text{S}_2\text{Cl}$ : 461.0998, found: 461.0984. **UV-Vis** ( $10^{-4}$  M,  $\text{CH}_3\text{CN}$ ),  $\lambda$ : 549 nm ( $\epsilon$  = 9092  $\text{M}^{-1} \text{cm}^{-1}$ ), 362 nm ( $\epsilon$  = 12 026  $\text{M}^{-1} \text{cm}^{-1}$ ), 240 nm ( $\epsilon_{\text{max}}$  = 17 463  $\text{M}^{-1} \text{cm}^{-1}$ ).

**1-Dicyanomethylene-3-(*N,N*-diethylamino)indene (10).**  $\text{PdCl}_2$ –(dppf) (5 mg, 0.004 mmol) was added with continuous stirring to a solution of **2** (30 mg, 0.106 mmol) in dry THF (15 mL) at room temperature under a nitrogen atmosphere and stirred for 30 min. Then TMEDA (0.21 mL,  $\rho$  = 0.770 g  $\text{mL}^{-1}$ , 1.420 mmol) was added and the reaction mixture cooled to 0 °C with an ice bath. To this mixture  $\text{NaBH}_4$  (20 mg, 0.530 mmol) suspended in THF (5 mL) was added dropwise and the mixture stirred for 2 h. Then the reaction mixture was poured into a chilled solution of HCl in water (50 mL HCl, 10% w/v, and 100 g ice). The aqueous phase was extracted with dichloromethane ( $3 \times 50$  mL). The combined organic extracts were dried ( $\text{Na}_2\text{SO}_4$ ) and the solvent evaporated. The residue was purified by flash chromatography (silica gel,  $3 \times 15$  cm), from hexane– $\text{CH}_2\text{Cl}_2$  7 : 3 to 1 : 4, obtaining compound **2** as a pink solid. Yield 8 mg (30%). Mp: 108–110 °C. **IR** (KBr,  $\text{cm}^{-1}$ ):



2920, 2197 (CN), 1603, 1591, 1527, 1465, 1434, 1230.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 8.15 (m, 1H, CH=), 7.41 (m, 1H, CH=), 7.36–7.31 (m, 2H, CH=), 5.4 (s, 1H, CH=), 3.94–3.44 (m, 4H,  $\text{CH}_2$ ), 1.41 (m, 6H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 162.59, 161.34, 137.74, 135.18, 130.47 (=CH), 130.40 (=CH), 123.78 (=CH), 123.04 (=CH), 116.71 (CN), 116.68 (CN), 96.08 (=CH), 58.32, 49.21–46.22 (m,  $\text{CH}_2$ ), 14.59–12.55 (m,  $\text{CH}_3$ ) ppm. **MS (EI)**  $m/z$  (%): 249 ( $\text{M}^+$ , 23), 234 (16), 220 (26), 206 (44), 193 (17), 178 (6). **Anal.**: Calc. for  $\text{C}_{16}\text{H}_{15}\text{N}_3$ . C: 77.08, H: 6.06, N: 16.85. Found: C: 76.89, H: 5.93, N: 16.60%. **UV-Vis** ( $10^{-4}$  M,  $\text{CH}_3\text{CN}$ )  $\lambda$ : 574 nm ( $\epsilon = 5505 \text{ M}^{-1} \text{ cm}^{-1}$ ), 534 nm ( $\epsilon = 10\,607 \text{ M}^{-1} \text{ cm}^{-1}$ ), 506 nm ( $\epsilon = 10\,230 \text{ M}^{-1} \text{ cm}^{-1}$ ), 324 nm ( $\epsilon = 9967 \text{ M}^{-1} \text{ cm}^{-1}$ ), 299 nm ( $\epsilon = 9819 \text{ M}^{-1} \text{ cm}^{-1}$ ), 232 nm ( $\epsilon_{\text{max}} = 24\,673 \text{ M}^{-1} \text{ cm}^{-1}$ ).

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