

# Newer optical-based molecular devices from older coordination chemistry †

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This short review illustrates how the wealth of receptors and ligands available within coordination/supramolecular chemistry can serve as a launch-pad for producing information-handling optical-based molecular devices of various kinds: sensors, assay reagents, logic gates and even small-scale number processors. Such a diverse range of information-handlers allows the addressing of problems in different areas from a common viewpoint. The common viewpoint is strengthened further when we find that the design principles are quite small in number.

## Introduction

Not only does coordination chemistry have a rather rich tradition of designed associations between species,<sup>1</sup> its ideas were also embraced by the newer supramolecular science.<sup>2</sup> A number of the older products of coordination chemistry were applied by early analytical chemists to problems of metal ion determination.<sup>3</sup> With the current interest in molecular devices which process information in one way or another,<sup>4</sup> it is natural that such early applications would be extended.

Fluorescent or luminescent molecular devices particularly deal with information because light signals are so easily comprehended by people and machines.<sup>5</sup> Table 1 expands these devices according to the various manipulations of information that are available. Emphasis is laid in this instance on metal-containing lumophores, though all-organic counterparts are available under each category. We interpret 'device' according to the dictionary definition 'A thing designed for a particular

**Table 1** Molecular manipulation of information based on optical read-out

Action	Device	Example
Gathering	Sensor	<b>1</b> <sup>a</sup>
	Assay reagent	<b>2</b> <sup>b</sup>
	Antenna	<b>3</b> <sup>c</sup>
Transmitting	Wire	<b>4</b> <sup>d</sup>
Storing	Photochromic	<b>5</b> <sup>e</sup>
Displaying	Electrochromic	<b>6</b> <sup>f</sup>
Processing	Switch	<b>7</b> <sup>g</sup>
	Logic gate	<b>8</b> <sup>h</sup>
	Arithmetic system	— <sup>i</sup>

<sup>a</sup> O<sub>2</sub> sensor used for imaging air pressure on aerofoils.<sup>6</sup> <sup>b</sup> Used in immunoassays (after connecting to an antibody) for various clinical targets.<sup>7</sup> <sup>c</sup> Two concentric rings of 9 and 18 bacteriochlorophyll b units serve as the light-gathering component of the bacterial photosynthetic reaction centre.<sup>8</sup> <sup>d</sup> Transmits a large fraction of the input energy over the length of this large molecule.<sup>9</sup> <sup>e</sup> Demonstrator of photochromism.<sup>10</sup> All-organic cases<sup>11</sup> are more useful, however. <sup>f</sup> Electroluminescent display system<sup>12</sup> (when combined with electron donor and acceptor layers) used in e.g. automobile dashboards. <sup>g</sup> Electrochemically switchable luminescent system.<sup>13</sup> <sup>h</sup> INHIBIT logic gate operating with two inputs (H<sup>+</sup> and O<sub>2</sub>).<sup>14</sup> An all-organic case operating with three inputs and having a similarly long excited state lifetime is available.<sup>15</sup> <sup>i</sup> Metal-based examples are unknown at present. All-organic cases<sup>16,17</sup> are available, however.

function or adapted for a purpose'.<sup>18</sup> The most useful cases are those which directly solve real problems, and the examples in Table 1 are chosen on this basis. The longevity of the excited state is particularly important for several of the devices within Table 1. For instance, the long lifetime of **1** permits significant

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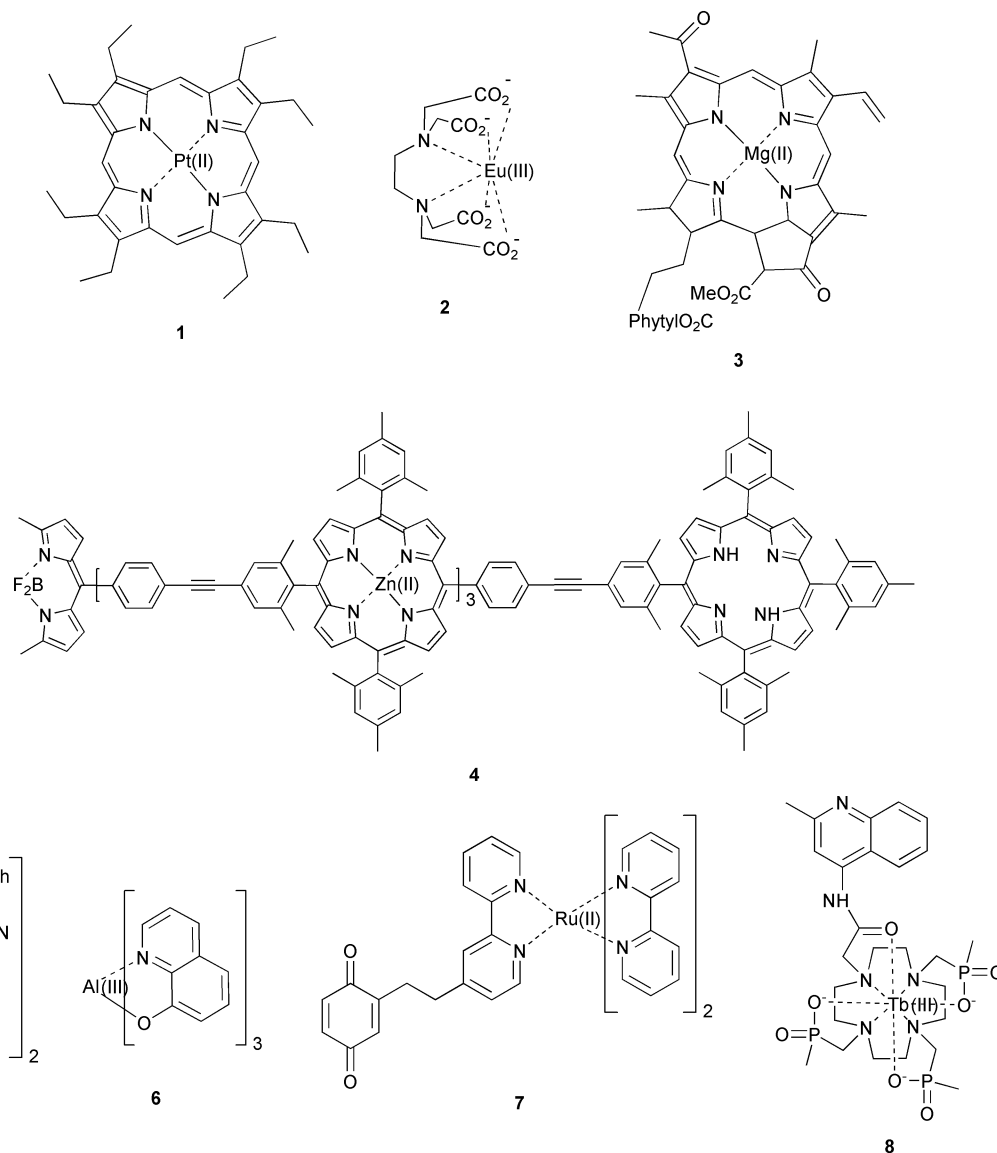


Front, left to right: Bernadine McKinney, Bridgeen McCaughan. Back, left to right: A. P. de Silva, Manel Querol-Sans.

*Bridgeen McCaughan is originally from a small town on the north Antrim coast of Northern Ireland famous for its annual fair, Ballycastle. She has been living and studying in Belfast for the past five years. She studied Chemistry at Queen's University, Belfast and spent three months working in the University of Prague, Czech Republic. She is currently working towards her PhD at Queen's University, Belfast in the field of fluorescence.*

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quenching of luminescence by collision with ambient levels of  $O_2$  such that the air pressure on aerofoil surfaces can be imaged in real time.<sup>6</sup> Similarly, the success of **2** in providing a non-radioactive alternative to well-established radioimmunoassay protocols for various clinical targets<sup>7</sup> is due to its long lifetime allowing time-resolution of its signal from matrix fluorescence.

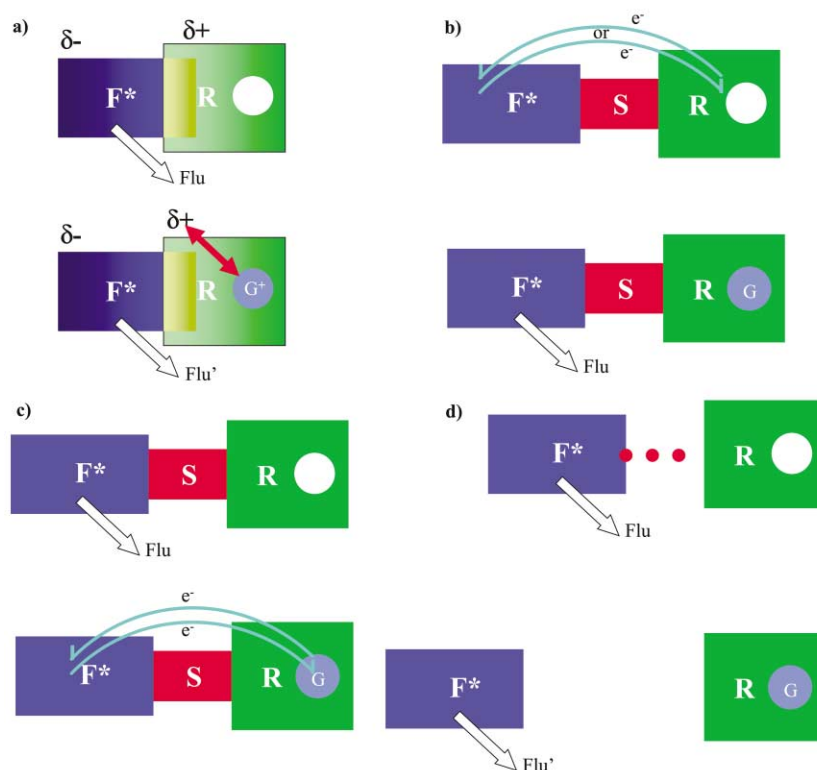
In this article we focus on optical sensing, assaying, logic and arithmetic devices, especially those where we see connections with our own efforts in these areas. The first of these devices involves the rather short process of going to a location (which can be of nanometric dimensions), measuring the local concentration of a target species in a selective, non-destructive, reversible and rapid manner, and then transmitting the data obtained to a human handler. Even this relatively short process faces considerable hurdles. If selectivity of target binding is achieved by maximizing the conditional formation constant,<sup>19</sup> the accompanying danger is the reduction of decomplexation rate with subsequent increase in operational time constant and intervals between serial measurements of usable data. Furthermore, localizing a molecular sensing device in a chosen micro/nanoenvironment is a challenge in itself.<sup>20</sup> However the situation is anything but gloomy because the issue of useful data transmission from the molecular device on command is neatly achieved by simple optical, and especially luminescent, spectroscopic methods.<sup>21</sup> Even a single molecular sensing device has been operated successfully,<sup>22</sup> though certain constraints seem unavoidable at present.

Molecular logic and arithmetic devices have a far shorter history than their sensing cousins and hence it should be no surprise that their usefulness is far less. In fact, the question has been posed publicly whether they are useful at all.<sup>23</sup> We believe this is a premature judgement especially when sensors are recognized as being simple logic devices from some viewpoints.<sup>4c,24</sup> Also the important point has been made, most eloquently by the Bolognese photochemists,<sup>25</sup> that molecular logic at least encourages chemists to extend their imaginations beyond the conventional boundaries of their discipline.

### Sensor devices

Sensors for chemical species (as well as physical properties) continue to be in high demand because of existing and emerging needs from many areas of human activity, particularly concerning health and environment. This demand will not go away. It is therefore important that we molecular scientists provide a range of design bases for such sensors. If one design fails to satisfy a given need, probably another will.

A selection of the most popular designs<sup>26</sup> are laid out in Fig. 1. These diagrams are very general and encompass many individual chemical structures, a few of which will be discussed below. We note at the outset that the choice of fluorophore is available in a variety of excitation and emission colours. Similarly the receptor can be chosen to target a particular guest in a given solvent, within a given concentration range and in the presence of a given set of potential intereferents. These choices



**Fig. 1** Design principles of sensor devices based on a) ICT, b) PET, c) EET and d) microenvironmental perturbation within assemblies. We note that light absorption (rather than fluorescence emission) forms the more common communication channel in Frame a). The red double-headed arrow signifies an interaction induced by the guest species in this and subsequent Figs. We also note that Frame c) shows a simultaneous double electron transfer in opposite directions corresponding to the electron exchange mechanism of EET which is expected to be very efficient at short separation distances.

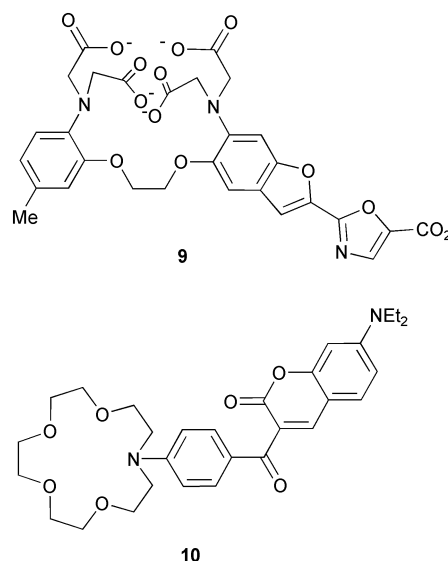
are of course subject to constraints such as availability of light sources, detectors and other optical components which are controlled by advances in optical physics and engineering. Similarly, the availability of receptors is dependent on developments in coordination and supramolecular chemistry. The choice of spacer, where necessary, is usually easy because these are invariably short (1 or 2 carbon atoms).

#### Sensor devices based on ICT (internal charge transfer)

ICT [also called PCT (photoinduced charge transfer)<sup>27</sup>] systems represent the oldest sensors, since many venerable ion indicators fit in here. The absorptometric types are older still, in fact the earliest observations of acid/base-induced colour changes of natural materials may well be lost in the mists of history.<sup>28</sup> The mechanistic understanding is roughly summarized within Fig. 1a. A significant charge separation exists within the excited state of the fluorophore partly because of its integration with the receptor. A push-pull  $\pi$ -electron system is usually required to separate substantial charges. Then it is natural that guest arrival at the receptor will perturb the entire integrated  $\pi$ -electron system. So the fluorescence emission and excitation spectral signatures, as well as the absorption signature are altered. The degree of alteration is still difficult to predict.<sup>27</sup> In fact even the understanding of the smaller effects seen in the emission, as opposed to the excitation, spectra was only attained a mere decade ago.<sup>29</sup> Briefly, the positive pole of the ICT excited state repels the cationic guest sufficiently to cause de-coordination before the fluorescence photon emerges, *i.e.* the fluorescence signature is close to that of the guest-free state.

Perhaps the biggest successes of fluorescent ICT sensors lie not in chemistry but in cellular physiology. Sensing in the micrometer world was a virtual mission impossible until Tsien<sup>4a</sup> cleverly developed older receptors from coordination chemistry into sensors such as **9** to spy on intracellular  $\text{Ca}^{2+}$  as it goes

about its everyday business. The presence of two spectral signatures, one for the guest-free sensor and the other for the guest-bound case is a boon here. Observation at two wavelengths and ratioing the two intensities compensates for several unknown variables in the intracellular wilderness.



A more recent example is **10** due to Chen and Huang.<sup>30</sup> They find a remarkable selectivity for the environmentally critical  $\text{Pb}^{2+}$  in the fluorescence enhancement response. Related structures had been tested as sensors before but with no exceptional properties. The proposed 2:2 complex where the arylazacrown ether and the dicarbonyl act as ligation sites may set **10**'s behaviour apart. The latter ligation site is indicated by the  $\text{Pb}^{2+}$ -induced red shifts seen in the absorption spectrum. Though classifiable as an ICT system, **10** possesses several formal single

bonds in the extensive chromophore which can potentially twist to produce TICT excited states.<sup>31</sup> Valeur and Rettig<sup>32</sup> have previously pointed out such a possibility in not-unrelated sensors.

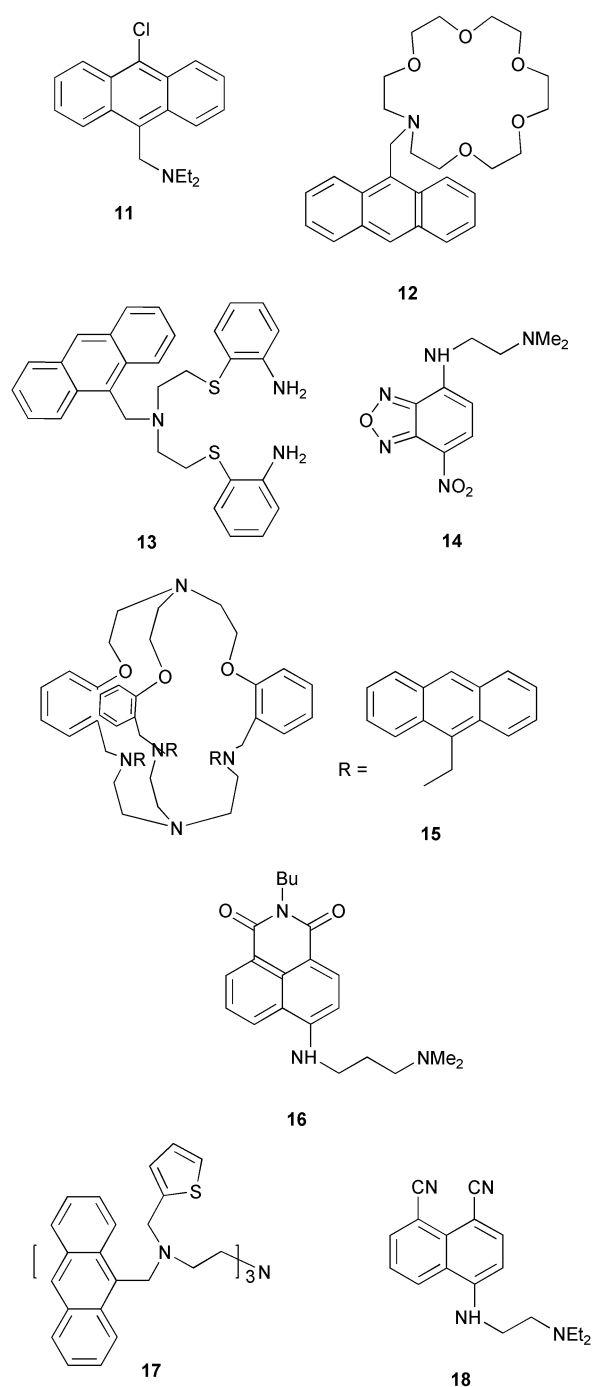
### Sensor and assay devices based on PET (photoinduced electron transfer)

PET systems are of a much more recent vintage, given the fact that the phenomenon of PET itself was only discovered in the 1960's.<sup>33</sup> The first sensor systems hark back to the 1970's<sup>34</sup> but we had the pleasure of generalizing them from the 1980's onwards.<sup>35,36</sup> Many laboratories have shared in the pleasure since.<sup>5,24,37</sup> Mechanistically, the fluorophore-receptor pair (Fig. 1b) is selected to allow rapid PET between them on the basis of simple electrochemical criteria. The rapidity is usually assured by sufficiently favourable PET thermodynamics and by using sufficiently short spacers. However the designer must also allow for the reversal of PET thermodynamics in the guest-bound situation. When the guest is  $H^+$ , this is easy to arrange. Guest-induced conformational changes in the receptor can be a valuable adjunct to purely electrostatic effects for the facilitation of sensing. The clearest result is a fluorescence switching 'off-on' effect caused by the guest. PET sensing systems are hard to beat for their sheer visual impact.<sup>38</sup> Given our favouritism towards this topic, a larger-than-usual collection of examples is discussed below.

It seems a long time ago when anthrylmethylamines such as **11**<sup>36</sup> were shown to be PET-based pH sensors and that elaboration of the amine to *e.g.* **12**<sup>39</sup> would give metal ion sensors. However it was clear throughout that we would need to be alert for this pH sensitivity. In fact the  $K^+$ -induced fluorescence enhancement of **12** was obtained in alkaline solution.<sup>39</sup> Kaur and Kumar's recent study of **13**<sup>40</sup> maintains this alertness. Their  $Cu^{2+}$ -binding experiments are conducted in aqueous MeCN buffered at pH 7. A FE (fluorescence enhancement) value of 8 is seen in response to 10  $\mu M$   $Cu^{2+}$  whereas several other transition (and post-transition) metal ions have no effect. Given  $Cu^{2+}$ 's notoriety as a fluorescence quencher, this is a very useful result which can be attributed to the suppression of the redox activity of the metal by the sulfide moieties. Several good sensors based on fluorescence quenching have been proposed recently,<sup>41,42</sup> but 'off-on' switching cases like **13** have a natural appeal. However, **13** is by no means unique in producing fluorescence enhancement with  $Cu^{2+}$  and related d-block ions. Samanta and his co-workers have published a string of papers on this very subject.<sup>43</sup> The plus point of Samanta's work is the structural simplicity of the receptor modules used in the sensors, *e.g.* **14** which are arylalkylamines. A possible minus point, though, is that the experiments are carried out in unbuffered non-aqueous solutions. Similar worries exist about the earlier compounds **15**,<sup>44</sup> contemporary **16**<sup>45</sup> and later **17**<sup>46</sup> and **18**.<sup>47</sup>

Protonation worries are less likely when aromatic amine-based ligands are incorporated into sensors – such as Tsien's **19** for  $Ca^{2+}$ <sup>48,49</sup> and our **20** for  $Na^+$ <sup>50</sup> (based on a Tsien receptor<sup>51</sup>) – and when pH-controlled aqueous solutions are employed. Tsien's sensors have succeeded handsomely in the cell physiology arena.<sup>4a</sup> **20** served as a lead compound for development of **21** which can now be found within blood analyzers found in hospital critical care units around the world.<sup>52,53</sup> It is important to note that Gunnlaugsson's **22**<sup>54</sup> shares both the sensing mechanism and the  $Na^+$  receptor with **21**.

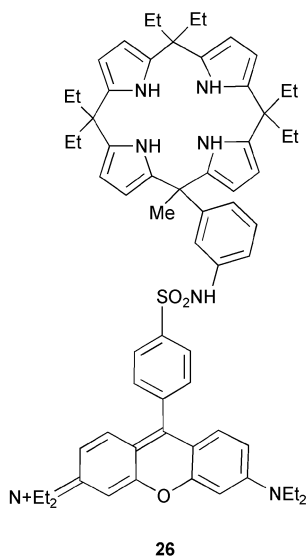
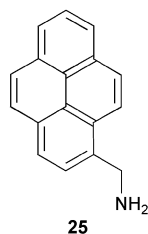
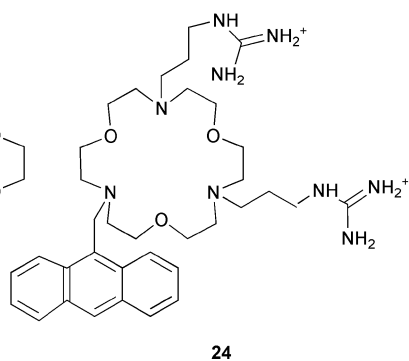
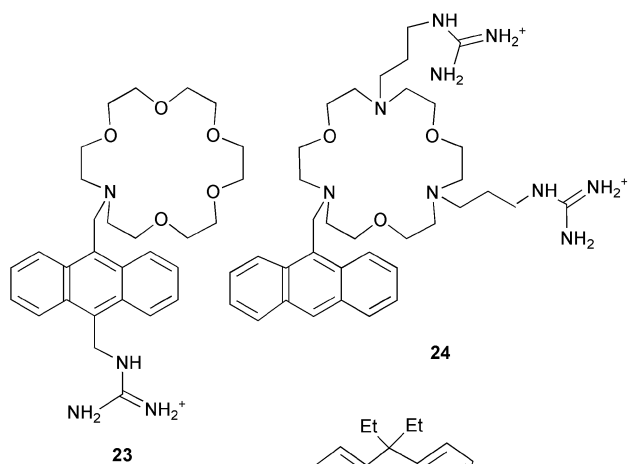
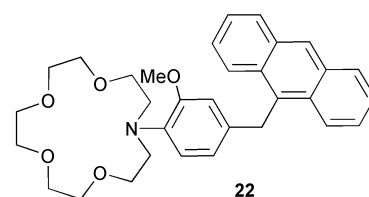
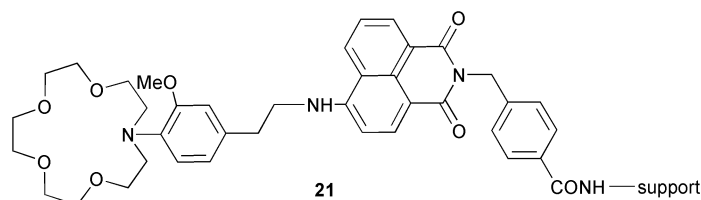
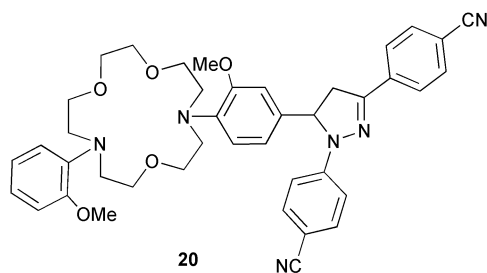
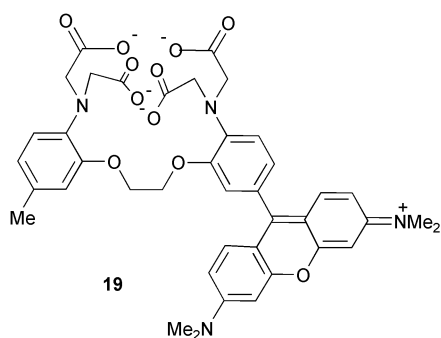
**12** has spawned many derivatives, one of which was our effort to sense amino acid zwitterions including the brain neurotransmitter GABA with **23**.<sup>55</sup> FE values of up to 3.5 were seen, though in aqueous methanol at pH 9.5. Now Sasaki *et al.*<sup>56</sup> replace two more oxygens in the macrocycle of **12** to get **24** and employ it in similar solvent and pH conditions. GABA gives a FE value of 2.2, not far from what was found



with **23**. The response to glycine is not dissimilar in the two cases either. In both cases, interference from alkali cations is unavoidable.

While fluorescent sensors for  $CO_2$  have been previously reported,<sup>57</sup> the polar aprotic solvent DMSO allowed Hampe and Rudkevich<sup>58</sup> to develop a nice 'off-on' switch. The primary amine in the PET switch **25** produces a 1:1 amine- $CO_2$  adduct. Eventually carbamic acid and carbamate salts (formed by proton transfer between carbamic acid and free amine) co-exist. Even  $N_2$  bubbling results in the loss of  $CO_2$  from the carbamic acid, whereas the carbamates will only return to **25** by refluxing in toluene. One way or another, reversible covalent binding of  $CO_2$  to **25** is thus demonstrated. Of course, reversible covalent binding of sugars have led to excellent PET sensors.<sup>59</sup>

Many readers would have noticed that this short tour has failed to mention a PET-based sensor for anions thus far. We put this right by featuring Sessler's **26**<sup>60</sup> where a calixpyrrole serves as the PET-active receptor for  $H_2PO_4^-$ . Refs. 61 and also 62 are relevant in this regard.



Though the discussion up to now has concerned reversible interactions between the molecular device and the guest species, there is still a role for systems which bind the guest once and for all. Such cases, if present in sufficient quantity, will extract the entire guest population rather than sampling it. These systems are straightforward assay reagents rather than sensors. Molecular assay reagents which measure total (rather than free) guest populations have formed the backbone of analytical laboratory practice for many years. They will also continue to be needed in situations where true sensors are unavailable.

While far older reagents for thiols<sup>63</sup> exist, our **27**<sup>64</sup> was the first case to be deliberately designed according to PET principles. The electron deficiency of the maleimide  $\pi$ -electron

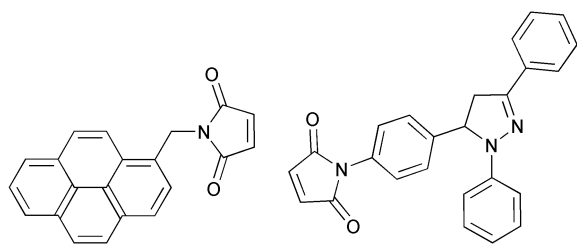
system allows PET from the fluorophore across the short spacer. PET stops when Michael addition of thiol to the maleimide drastically shortens its  $\pi$ -electron system. A recent case is Babu and Rajasekharan's **28**<sup>65</sup> where a spacer between the electron deficient C–C double bond and the fluorophore  $\pi$ -electron system is clearly visible. The spacer probably includes the  $sp^3$ -carbons as well as the phenyl ring, hence the moderate FE value of 6. An isomer **29** gives a higher FE presumably because the spacer is just the imide nitrogen (the junction of cross-conjugation). In fact **30** has an extreme fluorescence 'off-on' switching with thiols because of a similar situation as well as the probable presence of a TICT excited state.<sup>31</sup> NO is a highly topical guest for which fluorescent PET reagents have been recently developed with the most biologically successful cases like **31**<sup>66</sup> coming from Nagano's laboratory. Plater<sup>67</sup> has also provided another nice example **32**. Though mechanistically and behaviorally different, Lippard's **33**<sup>68</sup> has to be mentioned here.

A useful recent case is a PET reagent **34**<sup>69</sup> for peroxyacetic acid – an important bleach/disinfectant – from Imai's laboratory. This is a rare case where the PET occurs solely from an aliphatic sulfide as the donor. PET involving mixed donors including sulfur are known.<sup>70,71</sup> Of course, reaction of the sulfur centre with the peracid converts the sulfide to a sulfoxide and the PET possibility disappears. Our sulfide-based PET system **35**<sup>72</sup> is quite similar in delivering very high FE values when treated with excess hydrogen peroxide. **34** has been tested far more extensively<sup>69</sup> and detects less than picomole quantities of peroxyacetic acid with negligible interference from hydrogen peroxide.

An original Tsien PET sensor for  $Ca^{2+}$  has now been cleverly modified to **36** for the monitoring of protein kinase C (PKC) activity.<sup>73</sup> As with many of these hard molecular targets, the present assay is irreversible in that **36** is consumed during the monitoring process. Chen *et al.*<sup>73</sup> have designed a peptide-based species, where PKC will cause phosphorylation of a terminal alcohol to generate a  $M^{2+}$  receptor site composed of the two original carboxylates and the newly created phosphate. So the fluorescence enhancement mechanism is largely preserved. They insert a peptide-turn promoting linker such as *N*-methyl glycine between the peptide and the fluorophore so that the latter will not interfere with the recognition of the peptide by PKC but still enable the  $M^{2+}$ -induced switching 'on' of fluorescence. The result is a fluorescence enhancement factor of 3.6.

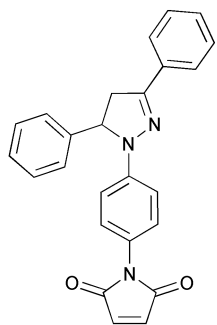
#### Sensor devices based on EET (electronic energy transfer)

EET is an older bimolecular photochemical phenomenon<sup>74</sup> than PET and one of its manifestations, FRET (fluorescence resonance energy transfer), has been a long-term servant of

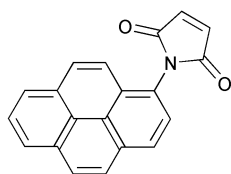


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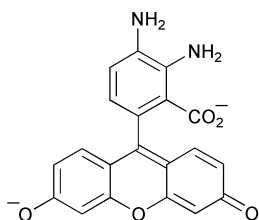
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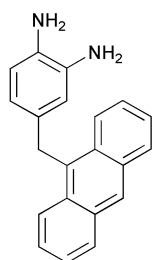
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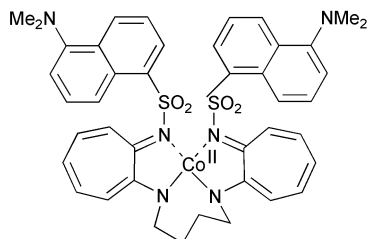
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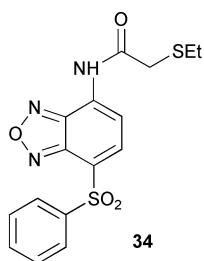
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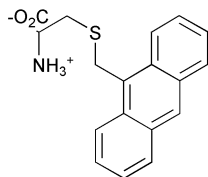
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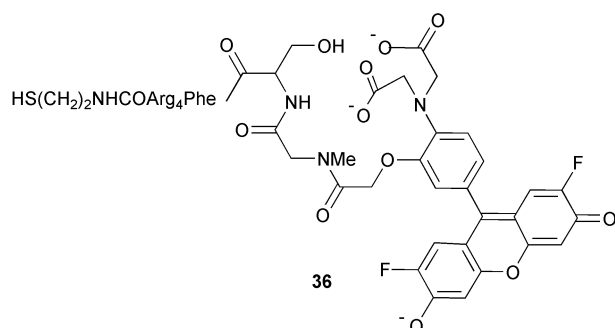
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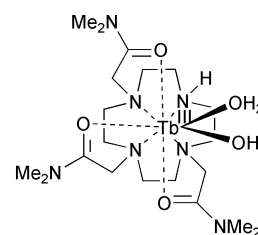
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analytical and mechanistic biochemists. One reason for the latter is that EET kinetically competes with fluorescence emission when most donor-acceptor pairs are separated by around 5 nm. Such large distances are useful in the context of big biomolecules. Of course, EET is also useful to detect association/dissociation reactions/phenomena of smaller molecules since the dissociated state is likely to concern separation distances of larger than 5 nm.

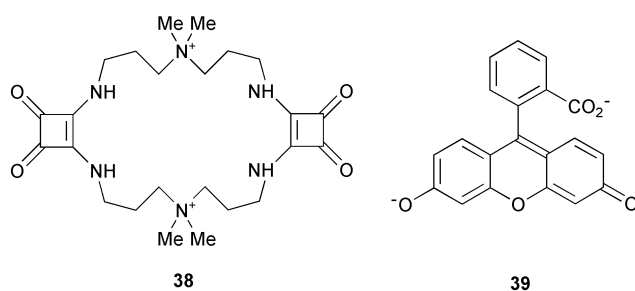
Electron exchange is a shorter-range version of EET which is one of the common reasons for the fluorescence quenching effects of transition metal ions, the other being PET. Electron exchange EET is illustrated in Fig. 1c. Several papers from the Fabbri laboratory involve this mechanism.<sup>75</sup> These authors have championed the persistence of fluorescence quenching in cryogenic glass media as a handy tool to distinguish EET mechanisms from possible PET versions.

EET can be put to good use in other ways too. Gunnlaugsson *et al.*<sup>76</sup> use Tb(III) complex **37** to detect salicylate (the biologically active metabolite of Aspirin®). **37** contains two labile metal-bound water molecules and no covalently attached organic chromophores for antennae. These molecules show negligible emission prior to the anion recognition since it is difficult to directly populate the excited states of the lanthanide ion. Salicylate attaches onto the Tb(III) centre by displacing the two labile metal-bound water molecules and allows the sensitisation of the lanthanide emission *via* EET.

### Sensor devices based on microenvironmental perturbation within assemblies

Microenvironmental perturbation of fluoro/chromophores within self-assembled systems has been heavily used in the probing of membranes.<sup>77</sup> However its targeted use in small-molecule sensing is due to the efforts of Anslyn,<sup>78</sup> Tonellato and Tecilla,<sup>79</sup> and recently, Fabbri.<sup>80</sup> As shown in Fig. 1d, the fluoro/chromophore associates with the receptor but the input guest can displace the former. Such competition scenarios hark back to immunoassay protocols.<sup>81</sup> The microenvironment of the fluoro/chromophore when free and when bound to the receptor can be quite different, especially when multiply-charged receptors are considered. So the fluorescence or absorption spectral signature is naturally affected upon guest arrival. Fabbri and co-workers<sup>80</sup> exploit the fluorescence quenching properties of receptors containing transition metals. Tonellato and Tecilla's approach<sup>79</sup> has differences in that the receptor-fluorophore assembly is arranged within a larger membrane system. An earlier case due to Arnold<sup>82</sup> has some relevance here. Overall, the removal of covalent bonding between the fluoro/chromophore and the receptor simplifies synthesis and encourages combinatorial exploration.

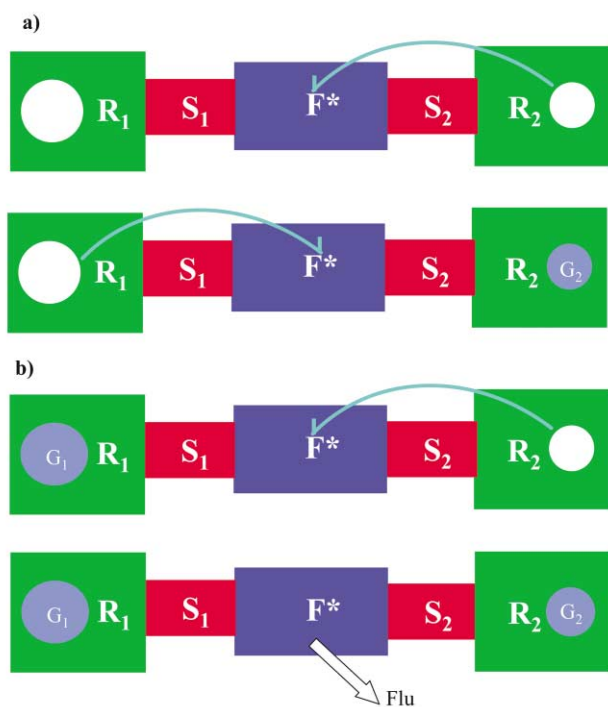
Ballester's **38**<sup>83</sup> is a particularly nice example from the recent literature which targets  $\text{SO}_4^{2-}$ . The binding is achieved with hydrogen bonds from the squaramide units and electrostatic attractions from the quaternary ammonium groups, aided of course by macrocycle effects. The sensor assembly also contains the anionic fluorophore **39**. The squaramide units cause PET to the fluorophore to produce fluorescence switching 'off'. The dianionic  $\text{SO}_4^{2-}$  fits the receptor **38** better than **39**. The displaced fluorophore **39** now gives a strong fluorescence signal.



## Logic and related devices

The opportunity to apply a given set of principles to two divergent research fields does not arise often. We count ourselves fortunate that sensor platforms turned out to be easily adapted to demonstrate molecular logic behaviour as far back as 1993.<sup>84</sup> While it is true that such demonstrations were quite different from what was on the wish list of the electronics industry, they clearly showed that the challenge of molecular computation could at least be addressed by bringing in chemical/biological ways of thinking. More recently, such thinking has even led to nice examples of multi-state systems and neuronal mimicry.<sup>85</sup> In fact, truly molecular electronic approaches to logic devices have only begun in recent years.<sup>86–88</sup> Even then, some of these require bulk metal connectors which sacrifices the molecular size-scale.<sup>89</sup> Other developments, such as all-optical logic<sup>90–92,17</sup> and nucleotide logic<sup>93,94</sup> have only had short histories. Of course synthetic DNA-based computation has been happening since 1994,<sup>95</sup> but the emphasis here is not on logic operations. It is in this context and background that we offer the following discussion. A nice introduction to logic devices from an electronic computation standpoint is available in ref. 96.

Fig. 2 outlines how sensing system arguments can be extended to logic systems by adding extra receptor modules. This means that extra guest input species will now elicit an optical response. A ‘receptor<sub>1</sub>–spacer<sub>1</sub>–fluorophore–spacer<sub>2</sub>–receptor<sub>2</sub>’ system is shown. A fluorescence signal emerges only when two appropriate guest inputs are received by the system to nullify the two possible PET paths arising from the two



**Fig. 2** Design principle of logic devices based on PET. Frames a) and b) together cover the full set of two-input conditions.

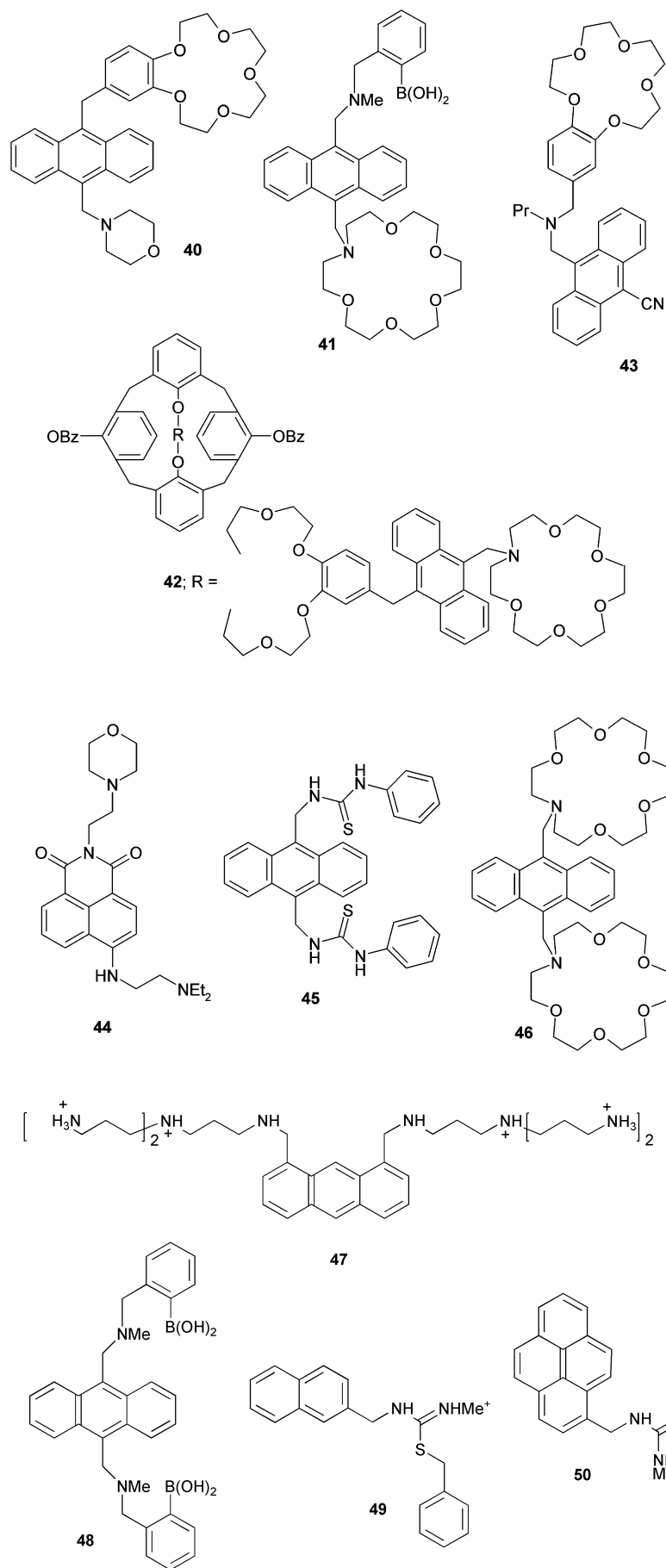
guest-free receptor modules. Our **40**,<sup>97</sup> James’ **41**<sup>98</sup> and Ji’s **42**<sup>99</sup> illustrate this AND logic behaviour. However, the ‘fluorophore–spacer<sub>1</sub>–receptor<sub>1</sub>–spacer<sub>2</sub>–receptor<sub>2</sub>’ system is older. In fact the first molecular logic gates in the primary literature are these, *e.g.* **43**.<sup>84</sup>

Some of the formats discussed in Fig. 2 can also find other uses. When we<sup>100</sup> found that only one of two available pathways was selected for electron transfer in the ‘receptor<sub>1</sub>–spacer<sub>1</sub>–fluorophore–spacer<sub>2</sub>–receptor<sub>2</sub>’ PET system **44**, it served as one of the simplest models of path-selectivity seen in the photosynthetic reaction center. We pictured this as being due to an ICT excited state being formed, the resulting internal electric field then directing the electron from the appropriate receptor. However Marcus and Gao<sup>101</sup> now analyze the phenomenon at a deeper level. Assuming that the molecule has a ground state and at least two excited states, they find that the effective orbitals are separated by very different numbers of bonds in the two alternative pathways. Since the separation distance is inversely related to the electronic coupling matrix, which in turn has a strong influence on the activation energy, this offers another explanation of the path-selectivity. We are delighted that **44** was selected for detailed theoretical analysis since the field of fluorescent sensors and switches has only had cursory attention of professional theorists. Even the applications of commonly available commercial software to such problems have been few and far between.

Gunnlaugsson’s **45**<sup>102</sup> illustrates the recent progress being made in the sensing of anions with ‘receptor<sub>1</sub>–spacer<sub>1</sub>–fluorophore–spacer<sub>2</sub>–receptor<sub>2</sub>’ PET systems where the two receptor units are identical. Oxoanion *e.g.* acetate binding to the *N*-aryl thiourea receptor units makes them more oxidizable. Hence PET occurs towards the fluorophore to give an oxoanion-induced fluorescence switching ‘off’. The availability of two thiourea units within **45** means that both need to be bound sequentially before the fluorescence quenching is complete. Of course, dianions *e.g.* pyrophosphate which span the distance between the two receptors can produce 1:1 binding stoichiometry. Our old **46**,<sup>103</sup> Czarnik’s **47**<sup>104</sup> and Shinkai’s **48**<sup>105</sup> are from the same gene pool which target cationic, anionic and neutral species respectively. PET sensors for anions based on charged thiouronium receptors like **49** are available from Kubo’s laboratory<sup>106</sup> which make an interesting comparison with **45**. Teramae’s **50**<sup>107</sup> also fits in neatly at this point. A reader has a right to feel that this paragraph should belong under the discussion of sensors and assay devices. We have chosen to discuss the material here because they are ‘receptor<sub>1</sub>–spacer<sub>1</sub>–fluorophore–spacer<sub>2</sub>–receptor<sub>2</sub>’ PET systems which gave rise to two-input logic behaviour which were not presented until this section. Such dilemmas illustrate again the entanglement of logic with sensing – a major take-home message in this article.

Akkaya’s **51**<sup>108</sup> shows fluorescence switching ‘off’ when Zn<sup>2+</sup> or H<sup>+</sup> binds to the bipyridyl unit. PET from the fluorophore is unleashed when the bipyridyl unit becomes more reducible after cation binding. This translates to fluorescent two-input NOR logic with Zn<sup>2+</sup> and H<sup>+</sup> as the two inputs. The same phenomenon with the same logic, inputs, receptor and mechanism can be found in our older **52**.<sup>15</sup> Though **51** is nice owing to the more complete switching (due to faster PET resulting from the shorter virtual C<sub>0</sub> spacer) and the longer communication wavelengths.<sup>108</sup> Fages’ **53**<sup>109</sup> also rightfully belongs here since it can be operated under a similar logic regime if required.

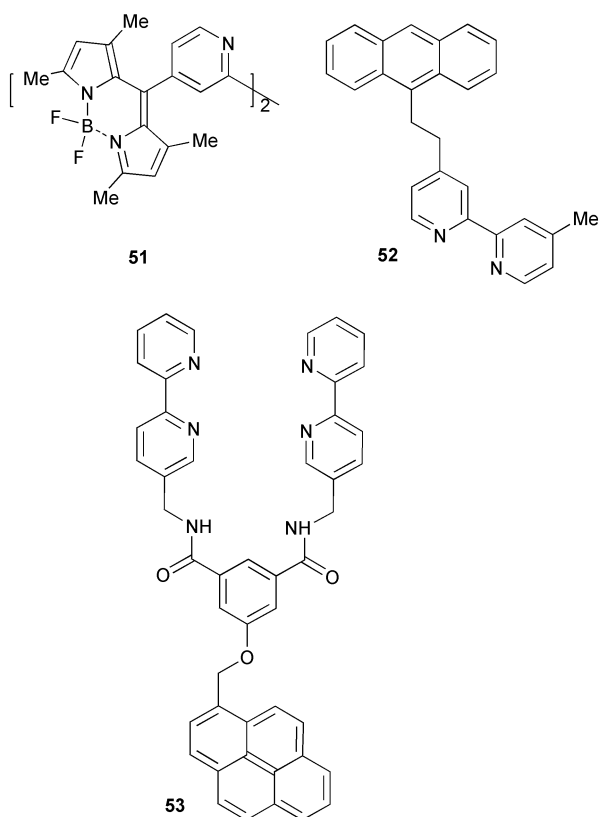
As Fig. 3 shows, putting two selective receptors on the opposite ends of a chromophore can give rise to an ICT excited state with significant charge separation. Then we have a situation in which application of the correct guest input to each receptor gives rise to opposite energetic effects on the excited state and hence opposite spectral shifts. This has been usefully examined so far only in the absorption spectra, though fluorescence versions will be very interesting subjects for the future. The ability



of two independent guest inputs to produce opposite spectral effects means that systems like **54**<sup>16</sup> show essentially the same absorption spectra whether both or none of the inputs ( $\text{Ca}^{2+}$

and  $\text{H}^+$ ) are applied. Further, application of one or the other input produces virtually the same high transmittance at the wavelength of the original absorption peak. In logic terms, this



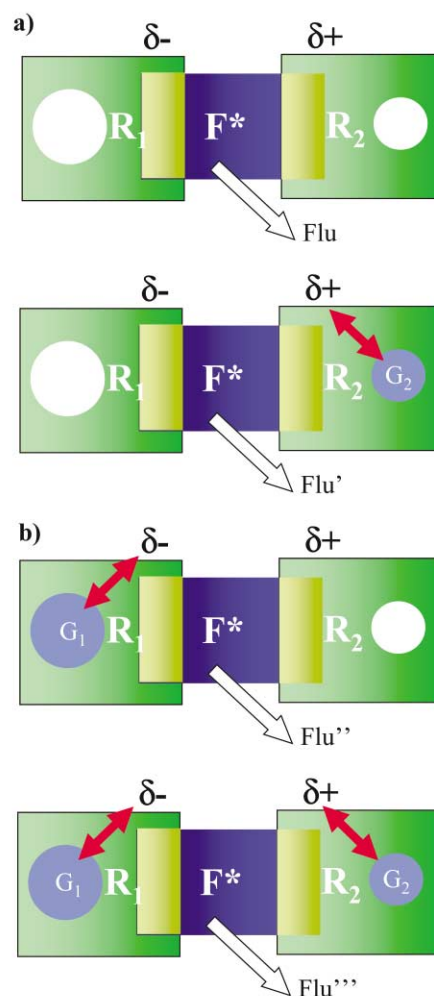


is the (two-input) XOR operation. An older XOR system is known<sup>110</sup> but its input pair have to be restricted to stoichiometric amounts and then they suffer mutual annihilation, making its operation difficult when arrayed with other gates.

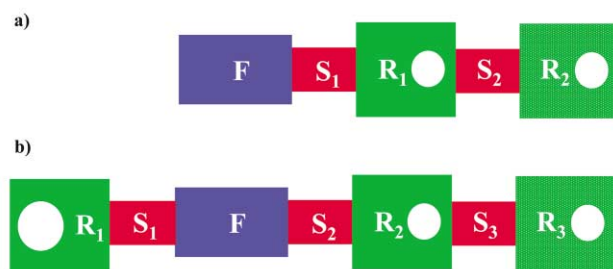
A related ‘receptor<sub>1</sub>–chromophore–receptor<sub>2</sub>’ system is Ataman and Akkaya’s **55**.<sup>111</sup> Alkali cation inputs choose the arylazacrown ether receptor to give a blue shift whereas lanthanide cations choose the calixdiquinone to produce a red shift instead. The indoaniline chromophore possesses sufficient ICT character in the excited state to cause the spectral shifts.

Tucker’s **56**<sup>112</sup> also belongs here since it performs the INH logic operation and because it contains two receptor units for a cation and an anion respectively. However the 4-nitroaniline moiety, which is the effective chromophore, interacts mainly with the urea receptor for F<sup>-</sup> rather than the benzocrown receptor for K<sup>+</sup>. F<sup>-</sup> causes a strong yellow coloration as the output signal by releasing electron density from the urea nitrogen for delocalization into the nitrophenyl system. K<sup>+</sup>’s arrival at the neighbouring benzocrown receptor electrostatically neutralizes the F<sup>-</sup> effect and the yellow colour fades.

One of the most complex PET-based switching systems designed thus far has emerged from S. A. de Silva’s laboratory.<sup>113</sup> **57** is a ‘receptor<sub>1</sub>–spacer<sub>1</sub>–fluorophore–spacer<sub>2</sub>–receptor<sub>2</sub>–spacer<sub>3</sub>–receptor<sub>3</sub>’ system (Fig. 4) where receptor<sub>1</sub> is occupied by Na<sup>+</sup> whereas receptor<sub>2</sub> and receptor<sub>3</sub> both receive H<sup>+</sup> though with different affinities. Mechanistically, the ‘fluorophore–spacer<sub>2</sub>–receptor<sub>2</sub>–spacer<sub>3</sub>–receptor<sub>3</sub>’ fragment can be discerned in fluorescent H<sup>+</sup>-driven ‘off–on–off’ switches like **58**,<sup>114</sup> **59**<sup>115</sup> and **60**.<sup>116</sup> Similarly, fragment ‘receptor<sub>1</sub>–spacer<sub>1</sub>–fluorophore–spacer<sub>2</sub>–receptor<sub>2</sub>’ – the other ‘parent’ – can be located in AND logic gates<sup>84</sup> like **40**<sup>97</sup> and **41**.<sup>98</sup> The fluorescence from **57** is strong only when the Na<sup>+</sup> concentration is high and the H<sup>+</sup> concentration is medium rather than high or low. So **57** is a Na<sup>+</sup>-enabled, H<sup>+</sup>-driven ‘off–on–off’ switch. The relative complexity of **57** is not only manifested in its function which is interesting in itself but also seen in the operation of three distinct PET processes which can each be controlled by ionic means. It is quite remarkable that all this is available in such a compact molecule.

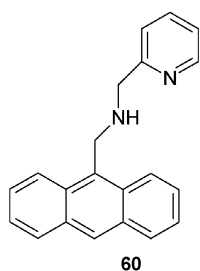
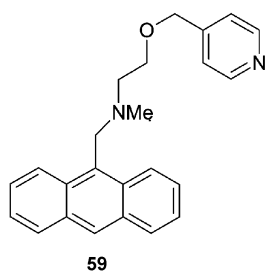
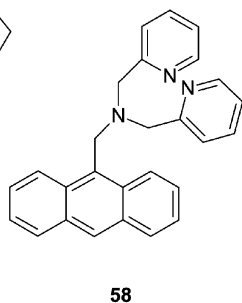
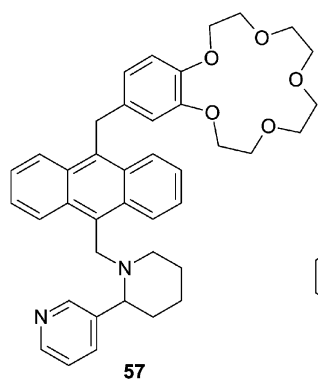
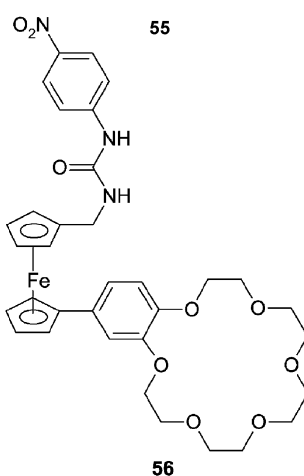
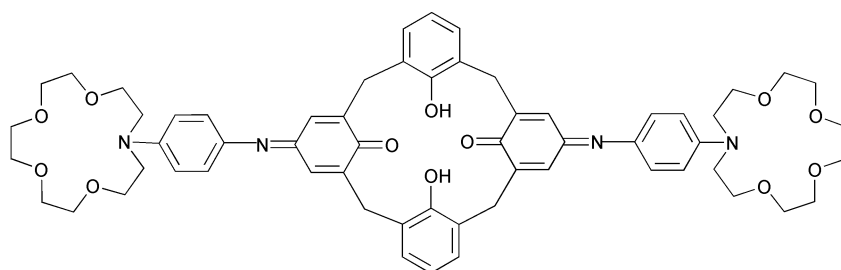
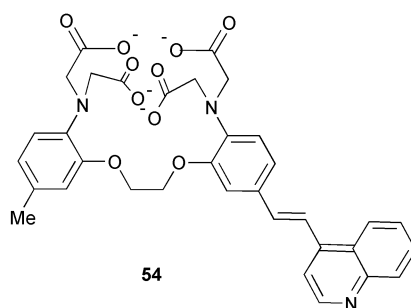


**Fig. 3** Design principle of logic devices based on ICT. Frames a) and b) together cover the full set of two-input conditions. We note that light absorption (rather than fluorescence emission) has been the more useful communication channel thus far, even though the version shown is likely to be more versatile.



**Fig. 4** Design principle of enabled ‘off–on–off’ devices based on PET exemplified by S. A. de Silva’s **54** [Part b)] as an outgrowth of simpler ‘off–on–off’ devices [Part a)].

Molecular logic takes an interesting turn when it turns out that simple ion indicators, including pH indicators that all chemistry students use, have logic gate properties.<sup>117</sup> Not only that, these humble indicators can simultaneously display multiple logic configurations. Even a simple indicator compound contains the four permissible single-input logic gates when it is examined at four colours. Here is the multiplexing power of light as compared with electric signals (displayed so well in the fibre optic communications revolution as compared to metal phone lines). The well-publicized area of quantum computation deals with superposition of quantum bit strings, *i.e.* the string 01 say will exist simultaneously as 01, 00, 11 and 10 in four parallel universes. So when the qubits are operated on by quantum logic gates all the strings are processed in parallel.



Now what do the ion indicators show? They show a superposition of logic gates. So simple indicators show a property which is related to but not the same as ideas in quantum computation. Thus we can generalize the idea of simultaneously

multiply-configurable logic within simple molecular systems. Cases like **54**<sup>16</sup> are more complex two-input versions, for example. However it is important to note that there are individual examples which can be interpreted in this way.<sup>91,118</sup> Such simultaneous configurability will allow optically functional molecular devices to enter areas where semiconductor-based electronic logic cannot easily go.

## Conclusion

It is clear that ligands and receptors emerging from coordination chemistry laboratories can be incorporated into molecular sensing and switching devices by combining the former with suitable chromo/fluorophores. A small set of design principles and photochemical mechanisms help designers to perform this combination as rationally as possible.

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