

# Chapter 12

## Circularly Polarized Luminescence from Intramolecular Excimers



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**Abstract** In this chapter, examples of circularly polarized luminescence (CPL) stemming from intramolecularly formed excimers will be reviewed. Emission from excimers has peculiar photophysical properties with respect to fluorescence of regular monomers. In addition, if the fluorophoric couple forming the excimer in the excited state is mounted on a chiral scaffold, a strong CPL can be usually observed. Examples of chiral scaffolds include oligopeptides, macrocycles, binaphthyl, and diaminocyclohexane derivatives. CPL from excimers has mainly been observed from pyrenes but other molecules are also able to give rise to such phenomenon, e.g., perylenes and 1,8-naphthalene monoimide. Excimer CPL can provide important information about the conformation of a molecule in the excited state and how it evolves depending on the environment (e.g., solvent and temperature) or external stimuli (e.g., light irradiation and cation addition). Moreover, thanks to the peculiar photophysical nature of excimers, the degree of circular polarization associated with excimer emission is usually much larger than the one associated with the absorption (electronic circular dichroism, ECD) for the same molecule. This allows to study chiroptical emission properties of molecules which are ECD-silent (ground state cryptochirality). As a whole, excimer CPL is an interesting and useful strategy to develop organic molecular systems endowed with bright and highly polarized luminescence.

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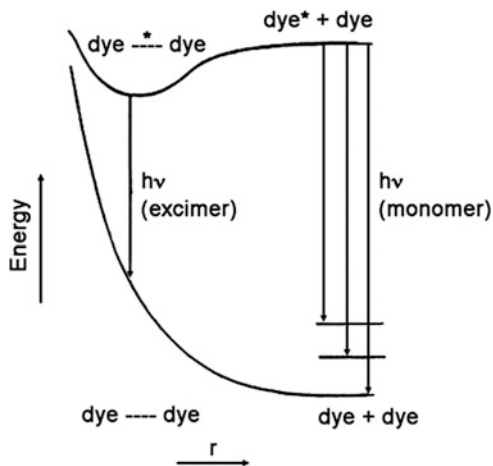
## 12.1 Introduction

According to IUPAC Gold Book an *excimer* is “an electronically excited dimer, ‘non-bonding’ in the ground state. For example, a complex formed by the interaction of an excited molecular entity with a ground state partner of the same structure [1].” Typically, in the realm of organic molecules, an excimer is formed between a pair of aromatic moieties ( $M$ ) loosely or non-interacting in the ground state. Upon excitation, a strong  $\pi$ - $\pi$  interaction takes place between the excited fluorophore ( $M^*$ ) and the one in ground state, generating thus an excited molecular complex, denoted as  $(MM)^*$  (Eq. 12.1) [2]. Emission from such species is called *excimer emission*. Such bands are red-shifted with respect to monomer emission and are broad and structureless, since the ground state is dissociative (Fig. 12.1) [3]. As for other chiral luminescent systems [4], excimer emission can be circularly polarized when using enantioenriched molecules or in non-racemic environments.



When dealing with purely organic fluorescent compounds, circularly polarized luminescence (CPL) activity is usually observed for intrinsically chiral and chirally perturbed fluorophores. In these cases, most of the time, a single CPL band is observed, if Kasha’s rule applies. This band corresponds to the fluorescence stemming from the lowest singlet excited state. If the geometry of the emitting excited state is not significantly different from that of the ground state, such a band has the same sign of the most red-shifted Cotton effect (which corresponds to the ECD of the same transition observed in absorption). Thus the  $g_{\text{lum}}$  factor is similar to the absorption dissymmetry factor ( $g_{\text{abs}}$ ) of the corresponding ECD transitions (in terms of order of magnitude and sign) [5]. On the other hand and by definition, an excimer is a state existing only in the excited state. As a consequence, CPL

**Fig. 12.1** General scheme of electronic states involved in excimer emission. Reproduced from reference [3] with permission from The Royal Society of Chemistry



properties of such transitions cannot thus be inferred from the ECD bands. For example, the sign observed for the first ECD and CPL bands are generally not related, indicating that the excimer geometry can be totally different to that of the ground state. In this way CPL gives new information which is complementary to that extracted from absorption spectroscopies.

To the best of our knowledge, in all the cases reported, the  $g_{\text{lum}}$  factor measured for excimer transitions is higher than  $g_{\text{abs}}$  by one or two orders of magnitude and typically falls in the range of  $10^{-2}$ . A possible explanation for such high  $g_{\text{lum}}$  can be the fact that an excimer is a single, extended intrinsically chiral fluorophore. As a comparison, we note that most of chirally perturbed chromophores/fluorophores or exciton systems display  $g_{\text{lum}}$  in the  $10^{-4}$ – $10^{-3}$  range. The  $n$ - $\pi^*$  transition from carbonyl groups in chiral molecules has typically a  $g_{\text{lum}}$  factor around  $10^{-2}$ , as it is magnetically allowed but electrically forbidden, but for the same reason very low quantum yields are observed in these cases [4]. In order to fully compare the overall polarization efficiency, it is convenient to take into account other relevant photophysical parameters beside dissymmetry factor. To this purpose, *circular polarization brightness* ( $B_{\text{CP}}$ ) was proposed (Eq. 12.2) in which  $\epsilon_{\lambda}$  is the extinction coefficient at the excitation wavelength,  $\Phi$  is the emission quantum yield, and  $B$  is the resulting brightness [6].

$$B_{\text{CP}} = \epsilon_{\lambda} \cdot \Phi \cdot \frac{|g_{\text{lum}}|}{2} = B \cdot \frac{|g_{\text{lum}}|}{2} \quad (12.2)$$

Considering, as a prototypical example, the circularly polarized excimer emission from pyrene, it is possible to elaborate the following numbers:  $\epsilon_{\lambda} \sim 4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ , quantum yield  $\sim 0.3$ ,  $g_{\text{lum}} \sim 10^{-2}$ . These numbers yield a  $B_{\text{CP}}$  around  $60 \text{ M}^{-1}\text{cm}^{-1}$ , which is around one order of magnitude higher than the values typical for most non-aggregated organic systems, and it approaches the figures of some lanthanide chiral complexes [7, 8].

Typical intermolecular excimer formation is a diffusion-controlled process. For this reason, excimer allied CPL is often observed in solid state or in aggregates [9] of non-racemic fluorophoric small molecules or oligomers and polymers. An effective strategy to alleviate this dependence is to allow intramolecular excimer formation by linking two or more fluorophores to a chiral molecular scaffold through suitable chains. In such cases, if the scaffold or the chains connecting the fluorophore units are scalemic, CPL can be observed with the typical  $g_{\text{lum}}$  factors discussed above.

In this chapter, we will review examples of CPL from intramolecularly formed excimers only, in different molecular systems and different contexts. A focus will be given on systems based on pyrene, perylene, and perylene bisimide and 1,8-naphthalene monoimide (NMI) moieties.

## 12.2 Pyrene-Based Systems

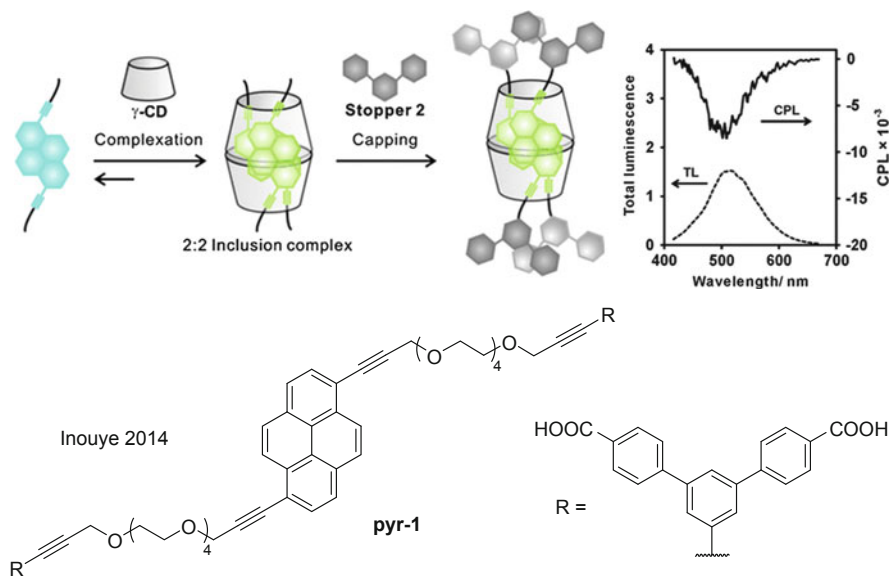
A privileged candidate for excimer formation is pyrene. The little overlap between the main  $S_0 \rightarrow S_2$  absorption transition with the emission spectrum minimizes the chance of fluorescence resonance energy transfer (FRET), thus ensuring a low excimer dissociation constant [10]. This often results in an intense excimer emission with the maximum around 480–500 nm. Tailored systems with defined geometries bringing pyrene moieties in close proximity to each other thus allow very intense excimer emission. If the scaffold on which the fluorophores are mounted is scalemic, or more generally the environment surrounding the targeted system, then excimer CPL can be observed depending on the geometry described by the mutual arrangement of the pyrene moieties in the excimer state.

The first observation of excimer CPL on pyrene was carried out by Kano and Sisido's groups in 1985 from a self-assembly of a pyrene dimer in the chiral cavity of a  $\gamma$ -cyclodextrin ( $\gamma$ -CDx) [11]. In this study, the authors were able to measure a strong CPL signal centered around 490 nm with a  $g_{\text{lum}}$  of  $11.2 \times 10^{-2}$ , thanks to the asymmetrically twisted configuration of the two pyrene molecules, acquired in the excimer state inside the  $\gamma$ -CDx chiral cavity. Interestingly, the dissymmetry factor measured in absorption for the first Cotton effect in the ECD spectrum was  $16 \times 10^{-5}$ , indicating very weak asymmetry of the arrangement of the two pyrenes in the ground state.

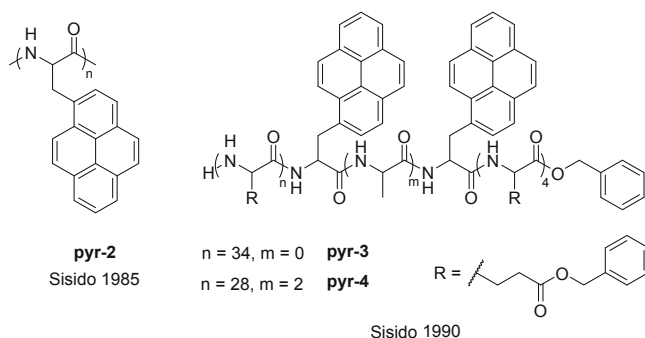
Recently, Inouye's group has taken advantage of the same concept [12]. Two substituted pyrenes bearing PEGylated chains to ensure an overall water solubility were included into a  $\gamma$ -CDx. Then, through Sonogashira couplings, 3,5-diaryl substituted phenyls were linked to the pyrenes at their extremities obtaining compound **pyr-1** (Fig. 12.2). By proceeding in this manner, the two pyrenes were locked physically inside the  $\gamma$ -CDx. A clear CPL associated to excimer emission was recorded (Fig. 12.2), with a  $g_{\text{lum}}$  of  $11.5 \times 10^{-2}$ , similar to that measured in the first experiment by Kano and Sisido (see above) [11].

### 12.2.1 Poly- and Oligopeptides Bearing Pyrene Units

In another context, that of synthetic polypeptides, pyrene CPL excimers were also studied to elucidate the changes of secondary/tertiary structures upon varying conditions, such as temperature and solvent. The chosen strategy was to functionalize different polypeptides with pyrene moieties and to exploit intramolecular formation of excimers to obtain information on the folding in different conditions. Thanks to the chirality of the polypeptidic backbone, excimer CPL could be induced and measured. Importantly, as chiroptical signals are extremely sensitive to the surrounding environment, even minor changes in the secondary structure caused relevant changes in the CPL response.



**Fig. 12.2** Top: adopted strategy for inclusion of pyrene dimers in  $\gamma$ -CD $_x$  and CPL/total luminescence spectra measured in H<sub>2</sub>O (pH 9.5,  $C = 4.5 \times 10^{-5}$  M). Bottom: structure of the compound. Adapted with permission from reference [12]



**Scheme 12.1** Structures of pyrene-decorated polypeptides developed by Sisido

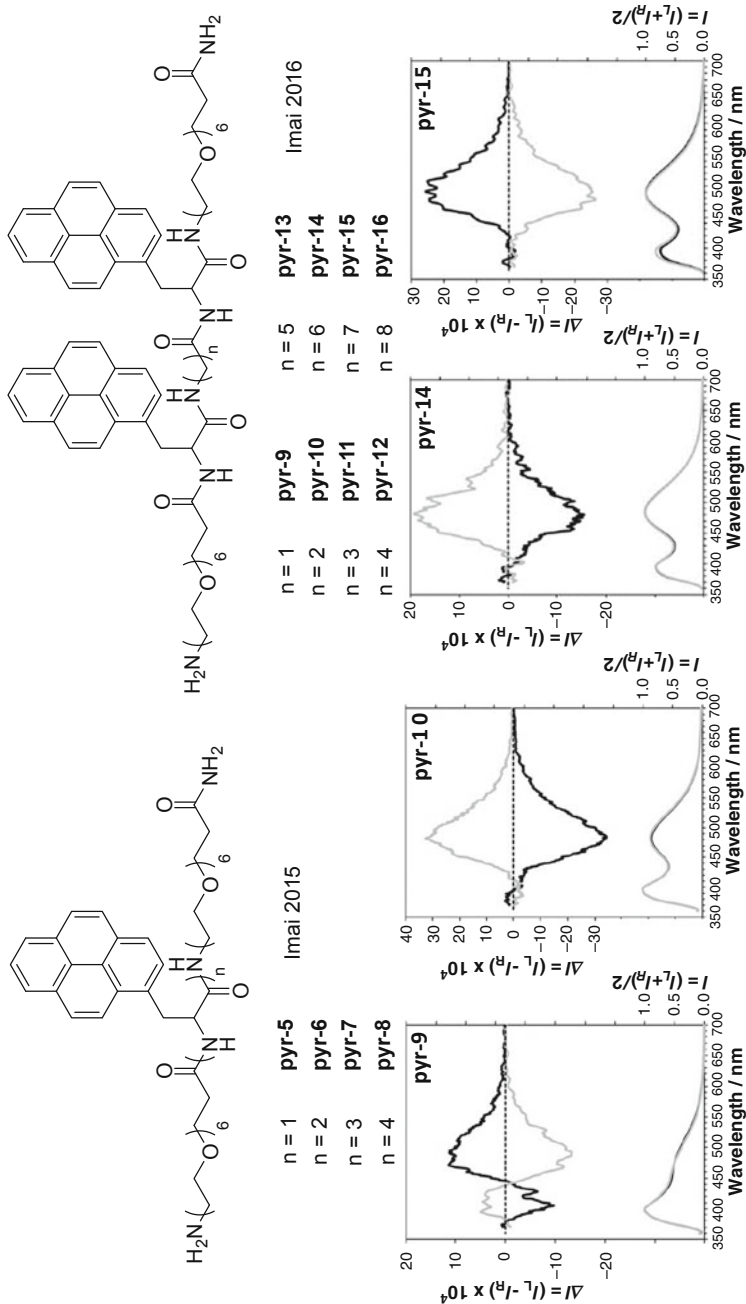
This approach was followed for the first time by Sisido et al. in 1985 [13]. They synthesized a poly-pyrenylalanine (**pyr-2**, Scheme 12.1) and studied the CPL in polar solvents, such as dimethylformamide (DMF) at variable temperature ( $6 \times 10^{-5}$  M). The  $g_{lum}$  vs. wavelength plot showed a sign inversion upon changing the temperature (from 3 to 60 °C) and even a bisignate profile for intermediate temperatures. These features suggest the presence of two sources for the excimer transitions: one stems from an apolar contribution due to exciton resonance ( $\text{Pyr}^*-\text{Pyr} \leftrightarrow \text{Pyr}-\text{Pyr}^*$ ), predominant at lower wavelengths, the second one comes from charge transfer resonance ( $\text{Pyr}^+-\text{Pyr}^- \leftrightarrow \text{Pyr}^--\text{Pyr}^+$ ), predominant at longer

wavelengths and stabilized in more polar solvents. These two components bring about different CPL signs, and the change of their relative contribution to the overall CPL spectrum at different temperatures thus explains the  $g_{\text{lum}}$  profile variations. In this case  $g_{\text{lum}}$  and  $g_{\text{abs}}$  (measured on the first Cotton effect) are of the same order of magnitude ( $10^{-3}$ ).

Later, Sisido's group synthesized two similar polypeptides, namely **pyr-3** and **pyr-4** (Scheme 12.1) [14]. In these examples, high  $g_{\text{lum}}$  values of  $11.6 \times 10^{-2}$  were detected associated with an excimer situation; no CPL being otherwise allied with monomer emission. The sign of the CPL was related to the handedness of the helix, which in turn depended on the length of the peptidic spacer: negative for **pyr-3** and positive for **pyr-4**. In these cases, the handedness is the same in both ground and excimer states, as indicated by the sign of the ECD band at 349 nm (negative for **pyr-3** and positive for **pyr-4**). For **pyr-3** and **pyr-4**, the ECD and CPL were also studied in DMF ( $6 \times 10^{-5}$  M) and tetrahydrofuran (THF) at +20 and  $-40$  °C [15]. As a first observation, the authors noticed that the  $g_{\text{lum}}$  values were constant over the whole emission band, which is consistent with only a single excimer configuration being present in each polypeptide. As a second observation, the signs of  $g_{\text{lum}}$  were opposite for **pyr-3** and **pyr-4** suggesting configurations with opposite screw sense in the two cases. For **pyr-3** specifically, a decrease of  $g_{\text{lum}}$  value, from  $11.2 \times 10^{-2}$  to  $0.4 \times 10^{-2}$ , was observed in DMF upon lowering the temperature from +20 to  $-40$  °C; a similar behavior occurring in THF although less pronounced. This suggests that a major conformational change occurs in the  $-40$  to +20 °C range.

More recently, other pyrene-decorated peptides bearing 1, 2, 3, or 4 pyrene moieties, **pyr-5–pyr-8**, were prepared and investigated by the group of Imai (Fig. 12.3) [17]. In  $\text{CHCl}_3$  ( $10^{-4}$  M), a low  $g_{\text{lum}}$  value of  $11.9 \times 10^{-4}$  was observed for **pyr-5** associated with the monomer fluorescence, while the dipeptide **pyr-6** showed the highest dissymmetry factor,  $11.1 \times 10^{-2}$ , allied with excimer emission. This latter  $g_{\text{lum}}$  value is 240-fold higher than the corresponding  $g_{\text{abs}}$  ( $\sim 10^{-5}$ ), while in the former case, in which no excimer occurs, the  $g_{\text{abs}}$  and  $g_{\text{lum}}$  are of the same order of magnitude.

Furthermore, Imai and collaborators prepared several other peptides bearing two pyrene moieties spaced by chains with different number ( $n$ ) of methylene spacers, allowing the authors to study the relationship between chiroptical properties and spacer lengths (**pyr-9–pyr-16**, Fig. 12.3) [16]. The sign of CPL associated with excimer emission underwent a sign inversion going from  $n = 1$  to  $n = 2$  (**pyr-9** and **pyr-10**), showing a sort of odd–even effect, and from  $n = 6$  to  $n = 7$  (**pyr-14** and **pyr-15**, see Fig. 12.3). On the other hand, the first Cotton effect, as shown in the ECD spectrum, did not show any sign inversion, revealing a completely different geometry of the ground and excited excimer states, confirming again the complementary nature of ECD and CPL when excimer states are at play. The maximum  $g_{\text{lum}}$  was recorded for  $n = 3$  (**pyr-11**,  $g_{\text{lum}} = 0.8 \times 10^{-2}$ ). In all instances,  $g_{\text{lum}}$  values were 1 to 2 orders of magnitude higher than the corresponding  $g_{\text{abs}}$  factors ( $10^{-3}$ – $10^{-4}$ ). With **pyr-12** ( $n = 4$ ), CPL sign inversion was also observed going from relatively apolar chlorinated solvents, such as  $\text{CHCl}_3/\text{CH}_2\text{Cl}_2$ , to polar ones



**Fig. 12.3** Top: structures of pyrene-decorated polypeptides developed by Imai's group. Bottom: selected examples of CPL and fluorescence (D-isomers in black, L-isomers in gray) measured in  $\text{CHCl}_3$  ( $10^{-4}$  M). Adapted with permission from reference [16]

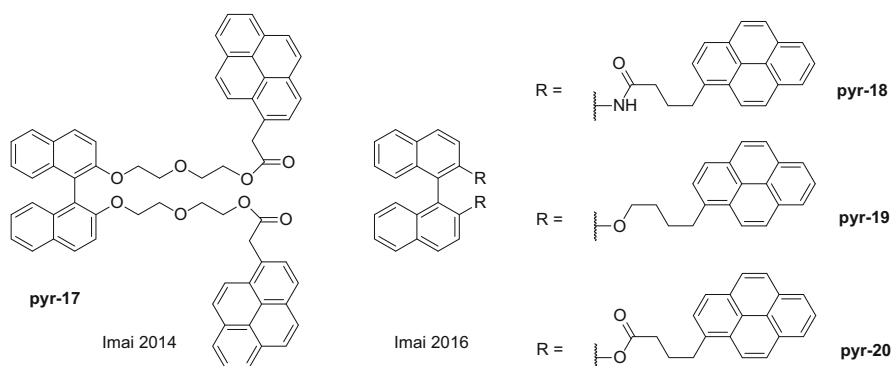
[Methanol (MeOH)/DMF/N-methyl-2-pyrrolidone (NMP)/dimethylacetamide (DMAc)], while no major changes occurred in the ECD spectra [18].

### 12.2.2 Ground State Cryptochirality and Excimer CPL

As the polarization effects on excimer bands can be higher than the ones in absorption by orders of magnitude, it is possible in some cases to specifically detect a CPL band even when the ECD is extremely small or non-detectable. This behavior is clearly observed when the chirality is brought by stereogenic elements (centers or axes) positioned at a distance from the chromophore/fluorophore units. The ground-state of such systems can be then considered as “cryptochiral,” for which the chirality cannot be (fully) detected through absorption-based chiroptical techniques, but the molecular asymmetry becomes evident upon emission polarization. In principle, this peculiarity could open a door to applications in cryptography and steganography [19].

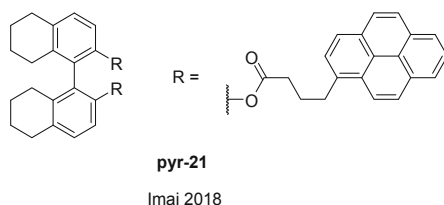
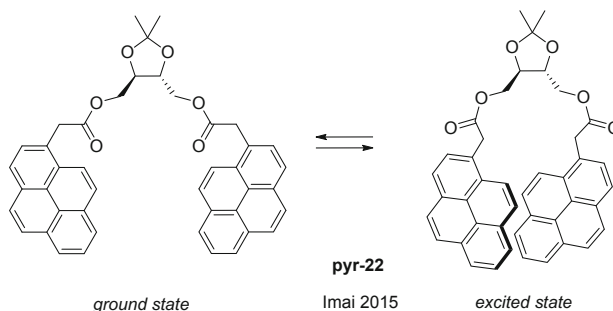
Imai et al. prepared **pyr-17** bearing two pyrene units linked to a core binaphthyl moiety through ethoxyethyl chains and ester linkages (Scheme 12.2) [20]. When dissolved in  $\text{CHCl}_3$  ( $10^{-3}$  M), this molecule displayed a  $g_{\text{abs}}$  of  $|3.8 \times 10^{-5}|$  at 344 nm while the excimer associated  $g_{\text{lum}}$  value was  $|7.8 \times 10^{-4}|$  (20.5 times higher). The excimer CPL, in comparison with ECD, displayed thus a quite higher sensitivity in revealing a long-distance chiral environment.

A similar behavior was observed for **pyr-18–pyr-20** for which the two pyrene moieties were linked to the central binaphthyl unit through amide, ether, and ester bonds, respectively (Scheme 12.2) [19, 21]. In these examples, the measured  $g_{\text{abs}}$  values were around  $10^{-5}$ , while the excimer associated  $g_{\text{lum}}$  factors were around  $10^{-3}$  ( $C = 10^{-5}$  M in  $\text{CHCl}_3$ ), with  $g_{\text{lum}}/g_{\text{abs}}$  ratios ranging from 17.9 to 62.5. Density functional theory (DFT) structures showed that the two pyrene moieties assume a nearly achiral T-shaped arrangement in  $S_0$  state, while in the excited state



**Scheme 12.2** Structures of pyrene decorated binaphthyl systems



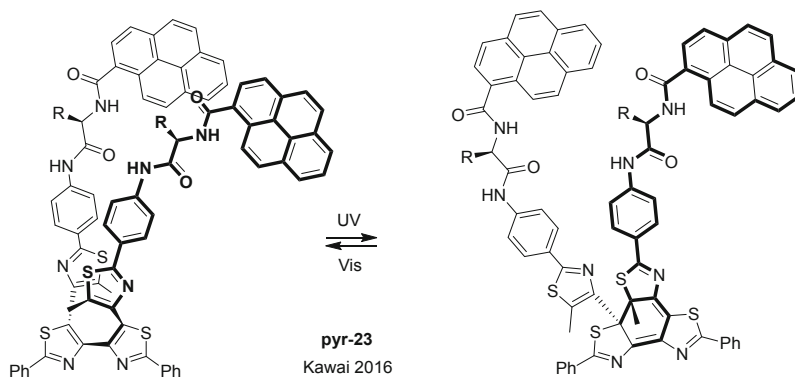
**Scheme 12.3** Structure of a pyrene-decorated octahydro-binaphthyl system**Scheme 12.4** Structure of a pyrene-decorated dioxolane system

they acquire a  $\pi$ -stacked skewed geometry. The same properties are retained as well by partially hydrogenated compound **pyr-21** (Scheme 12.3), analogous to compound **pyr-20** where the binaphthyl moiety is replaced by an octahydro-binaphthyl moiety [22].

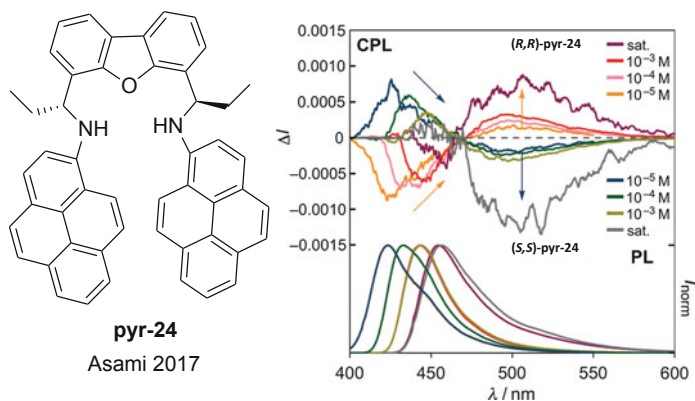
Imai's group developed a dioxolane, bearing two stereogenic centers, from which two pyrene moieties are connected through two  $-\text{CH}_2\text{OC}(\text{O})\text{CH}_2-$  ester chains (**pyr-22**, Scheme 12.4) [23]. The two pyrenes are thus located at the extremities of two floppy arms that dispose of a rather large conformational freedom. As such,  $\pi$ - $\pi$  interactions between pyrene units could not be detected in the ground state; the aromatic moieties assuming overall a T-shaped arrangement, as shown by DFT calculations and hence non-detectable ECD. On the other hand, a weak but observable excimer CPL band was measured with a  $g_{\text{lum}} = 18.9 \times 10^{-4}$  ( $C = 10^{-4}$  M in  $\text{CHCl}_3$ ), demonstrating again that a chiroptically active geometry, bound by  $\pi$ - $\pi$  stacking of the aromatic subunits, is obtainable in the excited state.

### 12.2.3 Excimer CPL in Chiroptical Switches

Thanks to the exceptional CPL activity associated with pyrene excimers, researchers have designed molecular systems that modulate their CPL response upon the occurrence of an external stimulus, such as light or the addition of ions. These systems are examples of so-called chiroptical switches.



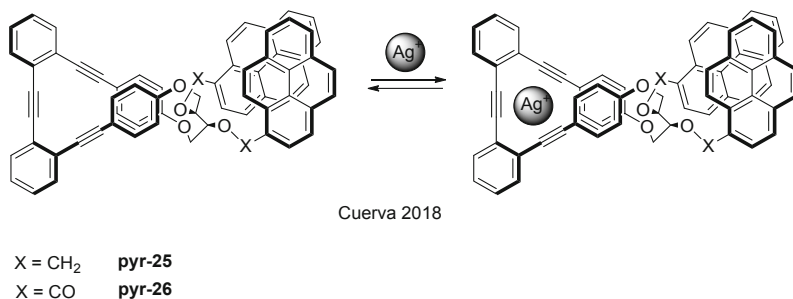
**Scheme 12.5** Tetrathiazole-based chiroptical switch reported by Kawai et al.



**Fig. 12.4** Concentration responsive pyrene-dibenzofuran molecule and CPL and total fluorescence as a function of **pyr-24** concentration in toluene. Adapted from reference [25] with permission from The Royal Society of Chemistry

Kawai's group reported a tetrathiazole-based compound which undergoes ring-opening/closure through a photoinduced reaction promoted by ultraviolet (UV) (for ring closure) or visible (for ring opening) light (**pyr-23**, Scheme 12.5) [24]. This transformation is accompanied by a large structural change. In the ring-open form, the two pyrene moieties are in close proximity giving rise to excimer-associated CPL with  $g_{\text{lum}}$  around  $10^{-2}$  ( $C = 1.7 \times 10^{-4}$  M in  $\text{CHCl}_3$ ). Upon photocyclization and the rigidification of the core three-dimensional (3D) structure, the two pyrene units are brought far apart, which results in a quenching of excimer CPL. Such light promoted CPL switching can be repeated over several cycles.

A molecule displaying concentration dependent CPL was developed by Asami and coworkers: [25] a dibenzofuran molecule linked to two pyrene moieties through a chiral chain (**pyr-24**, Fig. 12.4). Such compound shows a bisignate CPL profile, where monomer and excimer allied CPL have opposite signs (Fig. 12.4). Such sign

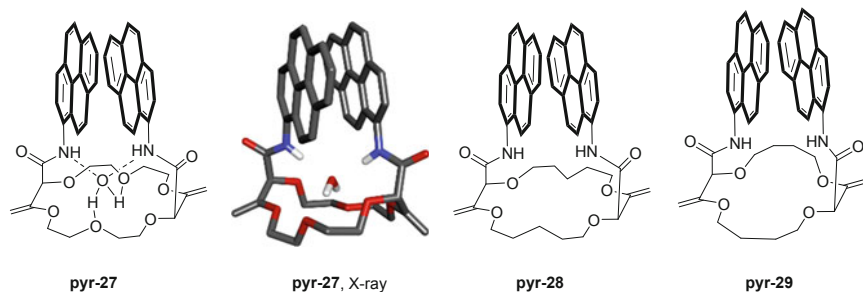
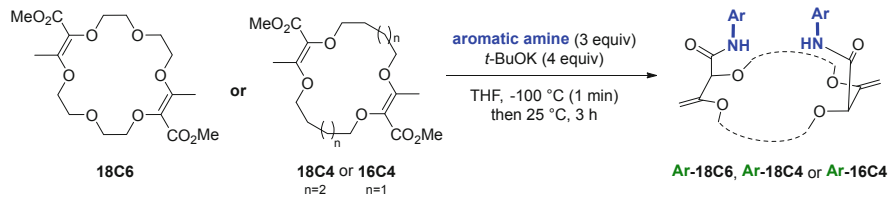


**Scheme 12.6** Pyrene-decorated ortho-oligo(phenylene)-ethynylenes showing Ag-induced chiroptical switch behavior

difference allows one to disentangle monomer and excimer contributions from the overall CPL spectrum ( $g_{\text{lum}} \sim 10^{-4}$  for the monomer and  $\sim 10^{-3}$  for the excimer). On the contrary, these two contributions are not clearly separable in the fluorescence spectra where the excimer is present as a broad tailing of the main monomer band (Fig. 12.4). Upon decreasing the concentration of **pyr-24** (from  $8 \times 10^{-3}$  M to  $1 \times 10^{-5}$  M in toluene, see Fig. 12.4), an increase in the monomer CPL  $g_{\text{lum}}$  was observed (from  $13.3 \times 10^{-4}$  to  $16.9 \times 10^{-4}$ ), while excimer allied  $g_{\text{lum}}$  showed only minor variations (from  $13.3 \times 10^{-3}$  to  $13.9 \times 10^{-3}$ ). This effect is probably due to different contributions to total luminescence and CPL from intra- and intermolecular excimer at different concentrations. On the other hand, ECD spectra at various concentrations did not show any variation of shape or intensity ( $g_{\text{abs}} = 16.2 \times 10^{-4}$ ), indicating that the ground state remains unaffected.

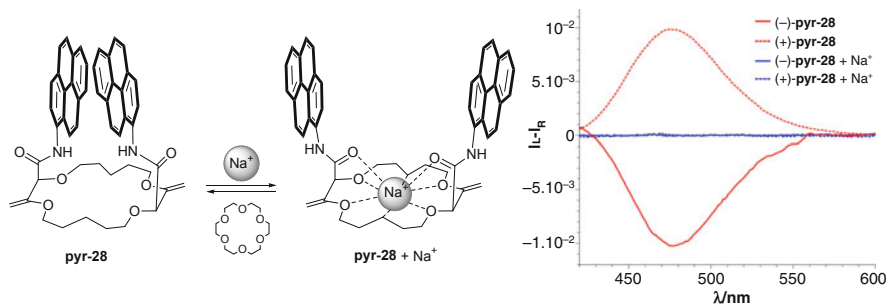
Recently, Cuerva et al. reported *ortho*-oligo(phenylene)-ethynylenes [26] decorated with two pyrene moieties (**pyr-25** and **pyr-26**, Scheme 12.6) [27]. These systems displayed again a bisignated CPL spectra ( $C = 10^{-5}$  M in CH<sub>2</sub>Cl<sub>2</sub>/acetone 95:5): the spectrum was dominated by the CPL emission associated to both phenylene-ethynylene moiety and to pyrene monomer at shorter wavelengths ( $\sim 400$  nm), while longer wavelength region ( $\sim 500$  nm) showed CPL allied to pyrene excimer emission with  $g_{\text{lum}} \sim 10^{-2}$ . Upon Ag<sup>+</sup> addition, the CPL profile is modified and the relative intensities of shorter and longer wavelength components change. In this way it was possible to quantify Ag<sup>+</sup> concentration, thanks to the determination of the ratio between  $\Delta I (I_L - I_R)$  at 400 nm and  $\Delta I$  at 500 nm. A CPL-based ratiometric probe sensitive to Ag<sup>+</sup> was thus established. Moreover, considering the ECD of **pyr-26**, the authors noticed that, upon Ag<sup>+</sup> addition, only the band related to oligo(phenylene)-ethynylene scaffold was affected (345 nm), while the bands related to pyrene absorption (387 nm) remained unaffected.

A different strategy was followed by the Lacour's group [28]. Thanks to a versatile synthetic approach in two steps only from common precursors, a family of polyether and polyether-like macrocycles was prepared carrying a wealth of different fluorophores (Scheme 12.7) [29]. In particular, 18C6, 18C4 and 16C4-type scaffolds were decorated with pyrene units through amide bonds (**pyr-27**–**pyr-29**, Scheme 12.7). These molecules displayed very intense excimer emission



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**Scheme 12.7** Straightforward synthesis of chiral functionalized macrocycles and structures of pyrene-functionalized macrocycles



**Fig. 12.5** Reversible complexation of sodium cations by **pyr-28** and associated CPL spectra recorded in  $\text{CH}_2\text{Cl}_2$  ( $10^{-5}$  M). Adapted from reference [28]. Published by The Royal Society of Chemistry

(compared to monomer band) with an associated  $g_{\text{lum}}$  in the range of  $10^{-2}$ . The intensity of the excimer fluorescence is the result of the peculiar geometry of these systems, which brings the pyrene units in close spatial proximity (see the X-ray structure in Scheme 12.7). Moreover, upon cation addition (e.g.,  $\text{Ba}^{2+}$  or  $\text{Na}^+$  in acetonitrile or  $\text{CH}_2\text{Cl}_2$ , respectively), profound conformational changes occur. In particular, the carbonyl groups of the amides turn inward and the two pyrene moieties part away from each other. It results in a loss of excimer fluorescence and in a total CPL quenching (Fig. 12.5). If the cation is removed, excimer CPL is fully recovered. In the ECD spectra instead, a signature inversion of most bands is visible



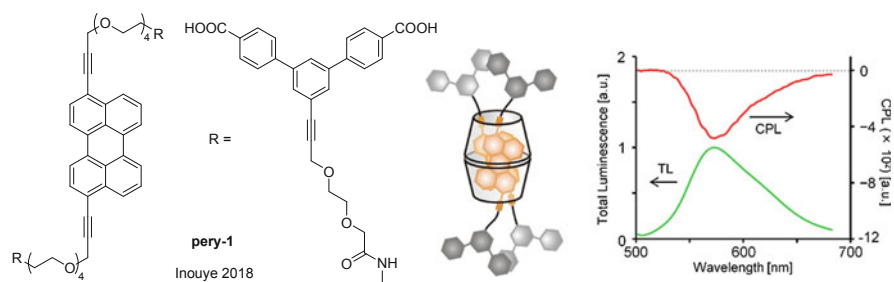
## 12.3 Perylene and Perylene Bisimide-Based Systems

Perylene and derivatives, such as perylene bisimides, are very well-established fluorophores, thanks to versatile access routes, very high quantum yields with emission shifted to long wavelengths. Traditionally, in these systems, the excimer formation is less efficient than with pyrenes. It is usually observed as a broad tailing along with the very intense and vibronically structured monomer-centered emission. Despite this limitation, some studies have been reported for which relatively intense excimer CPL signals have been measured, in particular in the case of designed intramolecularly-formed excimers.

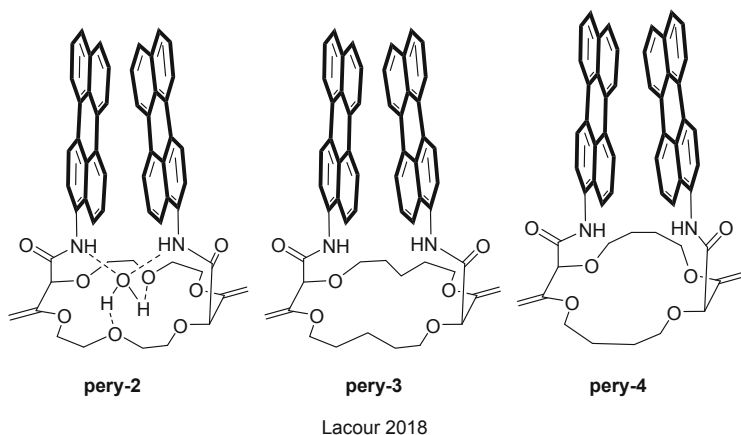
### 12.3.1 Excimer CPL from Perylene-Based Systems

**Pery-1**, prepared in an analogous manner to **pyr-1** (vide supra) [11], displays circularly polarized excimer fluorescence from perylene upon inclusion into a  $\gamma$ -CDx and subsequent capping via Sonogashira reactions (Fig. 12.7) [31]. For such a system, CPL with a  $g_{\text{lum}}$  of  $|2.1 \times 10^{-2}|$  was recorded (Fig. 12.7). This value is comparable to that measured for **pyr-1** in similar conditions [11].

Following the same synthetic strategy exploited for compounds **pyr-27**–**pyr-29**, Lacour and collaborators prepared diperylene derivatives **pery-2**–**pery-4** (Scheme 12.8) [28]. These systems displayed excimer fluorescence either as a principal component of the fluorescence spectrum (**pery-2** and **pery-3**) or as a tailing of the very intense monomer emission (**pery-4**). In the CPL spectra, two components are clearly visible; one associated to excimer emission with  $g_{\text{lum}}$  ca.  $|10^{-3}|$  and one allied to monomer fluorescence with a  $g_{\text{lum}}$  value, ca.  $|10^{-4}|$ , one order of magnitude lower. These two components have the same sign with **pery-2** and **pery-3**, but opposite signs for **pery-4**. In all these cases, CPL allows for a clear distinction between monomer and excimer contributions which is not obvious in fluorescence spectra. Upon  $\text{Ba}^{2+}$  (in  $\text{CH}_3\text{CN}$  for **pery-2**) or  $\text{Na}^+$  (in  $\text{CH}_2\text{Cl}_2$  for **pery-2**–**pery-4**) additions,



**Fig. 12.7** Structure of a substituted perylene included in  $\gamma$ -CDx and CPL/total luminescence spectra measured in  $\text{H}_2\text{O}$  (pH 9.5,  $C = 4.5 \times 10^{-5}$  M). Adapted with permission from reference [31]



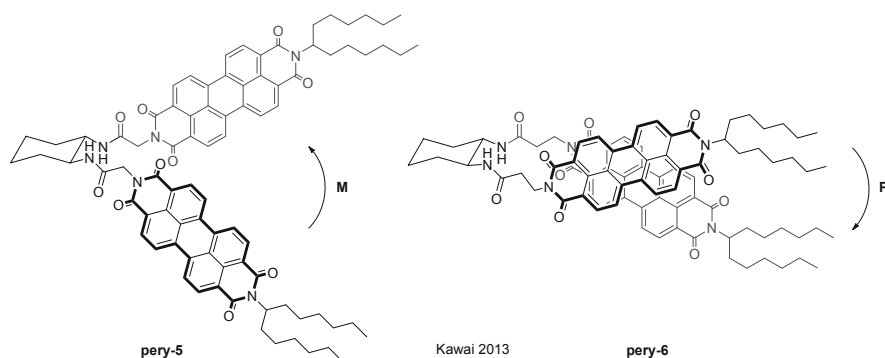
**Scheme 12.8** Structures of perylene-functionalized macrocycles

only monomer emission and its allied CPL remain, while excimer fluorescence and CPL are quenched in all cases. ECD spectra instead showed an exciton couplet structures in the visible range, which is slightly blue-shifted upon cation addition.

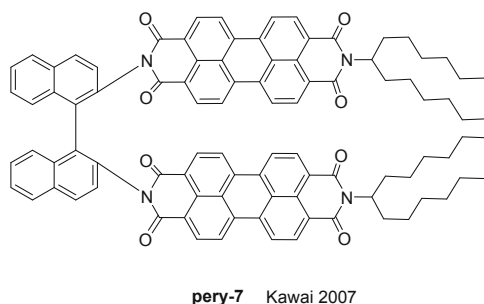
### 12.3.2 Excimer CPL from Perylene Bisimide-Based Systems

Kawai's group reported 1,2-diaminocyclohexane-based molecules linked to two perylene bisimide moieties through a glycine linker (**pery-5**) or a  $\beta$ -alanine spacer (**pery-6**, Scheme 12.9) [32]. A clear odd–even effect depending on the length of linker is visible in the ECD profile which shows exciton couplets featuring different signs in the two cases. In the case of **pery-5**, in  $\text{CHCl}_3$  as the solvent ( $C = 10^{-5}$  M), CPL profile showed a single band around 540 nm with the same sign as the first Cotton effect in the ECD spectrum with similar  $g_{\text{lum}}$  and  $g_{\text{abs}}$  values ( $g_{\text{lum}} \sim 16 \times 10^{-4}$  and  $g_{\text{abs}} \sim 14 \times 10^{-4}$ ). This indicates that such contribution stems from the weakly coupled lowest excitonic state. Compound **pery-6** showed the same CPL band. However, it displayed in addition an intense and broad band with opposite sign around 630 nm originated from the excimer state. As expected, this band displayed a much higher  $g_{\text{lum}}$  ( $18 \times 10^{-3}$ ) than that associated to the excitonic state emission.

On the contrary, when perylene bisimide moieties were mounted directly on a binaphthyl scaffold (**pery-7**, Scheme 12.10) [33], only an emission from the lowest excitonic state was observed in toluene, associated with a  $g_{\text{lum}}$  value of  $|2 \times 10^{-3}|$ – $|3 \times 10^{-3}|$  around 550 nm. No significant contribution from the excimer was visible, indicating that such structure does not allow for sufficient conformational freedom to obtain an effective overlap between the two fluorophores.



**Scheme 12.9** 1,2-Diaminocyclohexane/perylene bisimide adducts reported by Kawai et al.



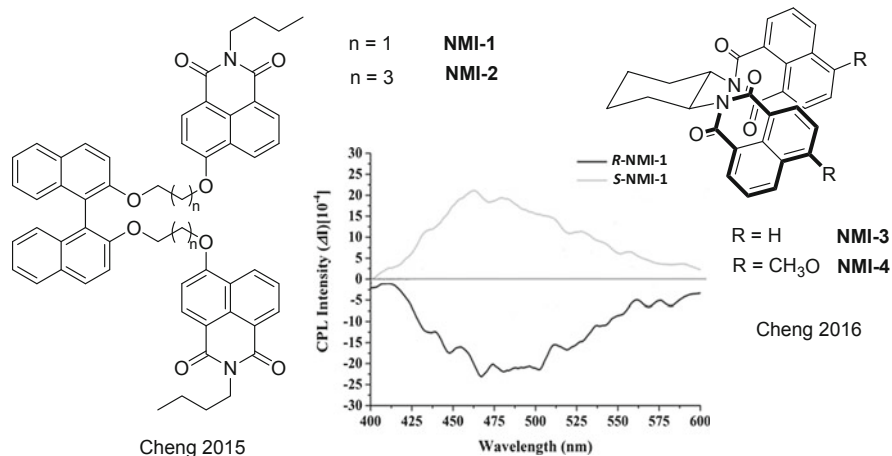
**Scheme 12.10** Binaphthyl/perylene bisimide system

## 12.4 1,8-Naphthalene Monoimide

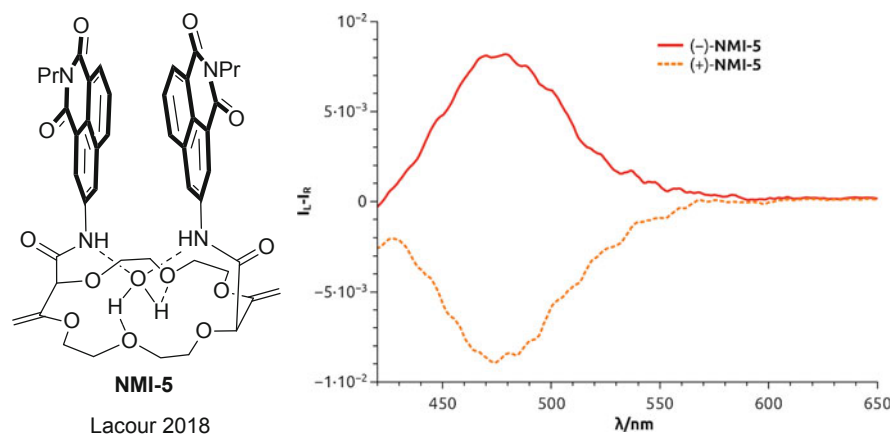
Another candidate for CPL excimer observation is the 1,8-naphthalene monoimide core, abbreviated NMI, which usually displays emission maxima in the 450–500 nm range. There are fewer reported examples of inter- and intramolecular excimer CPL with NMI and related structures, such as naphthalene bisimide [34]. Below, examples of NMI-based molecules that are able to display CPL allied to intramolecular excimer situations are described.

As in many of the above examples, it was possible to benefit from a central binaphthyl core and connect NMI fluorophores. Cheng et al. decorated a binaphthyl with two naphthalene monoimides (**NMI-1** and **NMI-2**, Fig. 12.8), linked through chains bearing either 2 or 4 methylenes [35]. Intramolecular excimer allied CPL was observed in THF solutions ( $C = 10^{-5}$  M) with  $g_{\text{lum}}$  of  $15.5 \times 10^{-3}$ – $16.1 \times 10^{-3}$  for **NMI-1** and  $13.0 \times 10^{-3}$ – $14.1 \times 10^{-3}$  for **NMI-2**. Upon addition of water, the molecules undergo aggregation. Inverted CPL with possible contributions from both inter- and intramolecular excimers and lower  $g_{\text{lum}}$  factors were observed. Similarly, when two NMI moieties were directly linked to a 1,2-diaminocyclohexane scaffold to obtain **NMI-3** and **NMI-4** (Fig. 12.8), the resulting derivatives showed excimer CPL in THF ( $C = 10^{-5}$  M) with  $g_{\text{lum}}$  values in the order of  $110^{-2}$  [36]. Again, in





**Fig. 12.8** 1,8-Naphthalene monoimide derivatives developed by Cheng et al. CPL spectra of NMI-1 (THF,  $C = 10^{-5}$  M). Adapted with permission from reference [35]



**Fig. 12.9** NMI-functionalized 18C6-macrocyclic and CPL spectra recorded in  $\text{CH}_3\text{CN}$ ,  $C = 10^{-5}$  M. Adapted from reference [28]. Published by The Royal Society of Chemistry

THF/water mixtures where aggregation takes place,  $g_{\text{lum}}$  factors remain of the same order of magnitude.

Finally, the Lacour's group was able to prepare **NMI-5** and observe excimer CPL with  $g_{\text{lum}} \sim |8 \times 10^{-3}|$  (Fig. 12.9), to be compared with a  $g_{\text{abs}} \sim |2.6 \times 10^{-4}|$ . In this compound, the donor group on the NMI moieties is attached at position 3 of the naphthalene subunit (and not 4 as it is usually the case), and this heteroatom serves as a linker to the 18C6-scaffold [28].

## 12.5 Conclusions

Chiral molecules bearing two or more fluorophores able to interact in the excited state and generate an emitting excimer induce fluorescence often with high quantum yield allied with highly polarized emission. Through this strategy, it is thus possible to maximize polarization output not only in terms of dissymmetry factor, but also in terms of circular polarization brightness [6], to an extent which is generally unsurpassed by most single organic molecule (i.e., non-aggregated) emitters. This field will benefit from further experimental efforts to produce and investigate new compounds. Moreover, computational analysis of excimer allied CPL could provide in the future better insight into the mechanism behind such phenomenon and help to design tailored systems. Unfortunately, to the best of our knowledge, no computational work has been reported so far on the topic. A possible difficulty lies in the optimization of excimer geometry, considering that such geometry exists only in the excited state, therefore no direct experimental structure is available for a straightforward check of the calculated one. In such cases, in fact, a correct geometry is necessary to reproduce emission [37, 38], and even more CPL [39], in a trustable way.

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