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Baroncini, M., Bergamini, G., Ceroni, P. (2017). Rigidification or interaction-induced phosphorescence of organic molecules. CHEMICAL COMMUNICATIONS, 53(13), 2081-2093 [10.1039/c6cc09288h].

*Availability:*

This version is available at: <https://hdl.handle.net/11585/585321> since: 2022-01-20

*Published:*

DOI: <http://doi.org/10.1039/c6cc09288h>

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Chem. Commun. 2017, 53, 2081 – 2093

The final published version is available online at:  
<https://doi.org/10.1039/C6CC09288H>

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# **Rigidification or interaction-induced phosphorescence of organic molecules: old concepts under new light**

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## **Abstract**

Phosphorescent materials are mostly based on metal complexes. Metal-free organic molecules usually display phosphorescence only in rigid matrix at 77 K. In the last few years, there has been an increasing interest for the design of organic molecules displaying long-lived and highly intense room-temperature phosphorescence, an extremely difficult task since these two properties are generally conflicting. This review reports the most recent and tutorial examples of molecules that are weakly or non-phosphorescent in deaerated fluid solution and whose room temperature phosphorescence is switched on upon aggregation. The examples are divided into two classes according to the mechanism responsible for switching on phosphorescence: (i) rigidification by crystallization or by encapsulation in a polymeric matrix and (ii) interaction with other molecules of the same type (self-aggregation) or different type by taking advantage of heavy-atom effects.

## **Introduction**

Phosphorescent materials are commonly used in organic light-emitting diodes (OLED), as well as in chemical and biological sensors, but because of a lack of practical, efficient and versatile metal-free organic phosphors, the range of usable materials is limited. Phosphorescence is indeed generally regarded solely as an inorganic or organometallic property. In the case of organic molecules, it is easily detectable in rigid matrix at 77 K, while at room temperature quenching by dioxygen is extremely effective because of the long lifetime of the phosphorescent excited state and it cannot be detected in air-equilibrated solution. However, phosphorescence of organic molecules is known since a long time.<sup>1-4</sup> In 1941 Lewis and his coworkers first suggested that the long-lived phosphorescence of fluorescein in rigid media derives from the lowest triplet state.<sup>5</sup> In 1944, Lewis and Kasha published the phosphorescence of a large series of aromatic molecules in rigid glasses at 77 K.<sup>6</sup> The first unequivocal demonstration of the fact that phosphorescence derives from a triplet state was made by Lewis and Calvin in 1945:<sup>7</sup> they demonstrated that the phosphorescent state of fluorescein in a boric acid glass at room temperature is paramagnetic. In 1955 Evans and coworkers reported that the lifetimes of phosphorescence and paramagnetic susceptibility are identical for triphenylene in boric acid glass at room temperature.<sup>8</sup>

In 1972 it was discovered that many salts of polynuclear carboxylic acids, phenols, amines, and sulfonic acids adsorbed on solid substrate like filter paper, silica or alumina exhibit strong phosphorescence at room temperature, with no evidence of quenching by dioxygen.<sup>9</sup> As expected, the spectra were similar to those of frozen solutions at 77K. In the following years, Turro reported solubilization of arenes in micellar aggregates as a way for the ready observation of phosphorescence at room temperature.<sup>10</sup> Then, different hosts,<sup>11</sup> like

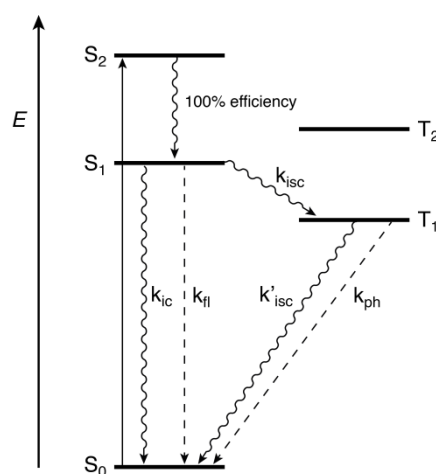
cyclodextrins,<sup>12</sup> zeolites,<sup>13</sup> and hemicarcerand<sup>14</sup> were used to induce room-temperature phosphorescence of organic molecules and this process was exploited as a powerful analytical tool.<sup>15</sup>

In the last few years, there has been a resurgence of interest towards the rational design and theoretical study of novel organic molecules weakly or non-phosphorescent in deaerated fluid solution and whose room temperature phosphorescence is switched on upon aggregation.<sup>16–21</sup> A better understanding of the mechanistic details involved in long lived luminescence in solid organic materials and general strategies for their preparation is of paramount importance for their application in electroluminescent devices, luminescent sensors and cell imaging materials.

The present review is focused on organic molecules which do not exhibit phosphorescence in deaerated fluid solution and whose room temperature phosphorescence is switched on either by rigidification of the matrix (crystallization or dispersion in a polymer matrix) or by aggregation and electronic interactions of the molecules among themselves or with the host matrix. Before presenting a selection of the most relevant examples from the tutorial point of view and their potential applications, it is worthwhile recalling a few elemental principles of electronic spectroscopy with particular focus on phosphorescence and the parameters affecting its efficiency and its time-decay. Interested readers can refer to several books for deeper discussions.<sup>22–24</sup>

## Phosphorescence

Phosphorescence is the radiative decay between electronic excited states of different spin multiplicity: it is a spin-forbidden process and it is thus intrinsically slower than the spin-allowed fluorescence process.



**Figure 1.** Schematic Jablonski diagram for a generic organic molecule: solid line for absorption, dashed line for emission processes and wavy lines for non-radiative processes.

To get better insights onto the phosphorescence and the other competing processes, we can refer to Figure 1 that depicts a schematic energy level diagram for a generic organic molecule. The ground electronic configuration of an organic molecule is usually closed-shell, so that, in most cases, the ground state is a singlet state (S<sub>0</sub>), and the excited states are either singlets (S<sub>1</sub>, S<sub>2</sub>, etc) or triplets (T<sub>1</sub>, T<sub>2</sub>, etc). In principle, transitions between states having the same spin value are allowed, whereas those between states of different spin are

forbidden, so that  $T_1$  excited state cannot be populated by direct absorption of light. The electronic absorption bands correspond to  $S_0 \rightarrow S_n$  transitions. When a molecule is excited to upper singlet excited states, it usually undergoes a fast and 100% efficient radiationless deactivation (internal conversion, ic) to the lowest excited singlet,  $S_1$  (Kasha's rule).<sup>25</sup> Such an excited state undergoes deactivation via three competing first-order processes: non-radiative decay to the ground state (internal conversion, rate constant  $k_{ic}$ ); radiative decay to the ground state (fluorescence,  $k_{fl}$ ); conversion to the lowest triplet state  $T_1$  (intersystem crossing,  $k_{isc}$ ). In its turn,  $T_1$  can undergo deactivation via non-radiative (intersystem crossing,  $k'_{isc}$ ) or radiative (phosphorescence,  $k_{ph}$ ) decay to the ground state  $S_0$ . The lifetime ( $\tau$ ) of an excited state, i.e. the time needed to reduce the excited state concentration by 2.718, is given by the reciprocal of the summation of the deactivation rate constants:

$$\tau(S_1) = 1 / (k_{ic} + k_{fl} + k_{isc}) \quad (1)$$

$$\tau(T_1) = 1 / (k'_{isc} + k_{ph}) \quad (2)$$

The orders of magnitude of  $\tau(S_1)$  and  $\tau(T_1)$  are approximately  $10^{-10}$ - $10^{-8}$  s and  $10^{-6}$ - $10^0$  s, respectively; while upper lying excited states  $S_n$ ,  $T_n$  exhibit much shorter lifetimes of the order of  $10^{-12}$  s, in agreement with Kasha's rule.

The quantum yields of fluorescence (ratio between the number of photons emitted by  $S_1$  and the number of absorbed photons) and phosphorescence (ratio between the number of photons emitted by  $T_1$  and the number of absorbed photons) can range between 0 and 1 and are given by the following expressions:

$$\Phi_{fl} = k_{fl} / (k_{ic} + k_{fl} + k_{isc}) \quad (3)$$

$$\Phi_{ph} = \eta_{isc} \times \eta_{ph} = k_{ph} k_{isc} / [(k'_{isc} + k_{ph}) (k_{ic} + k_{fl} + k_{isc})] \quad (4)$$

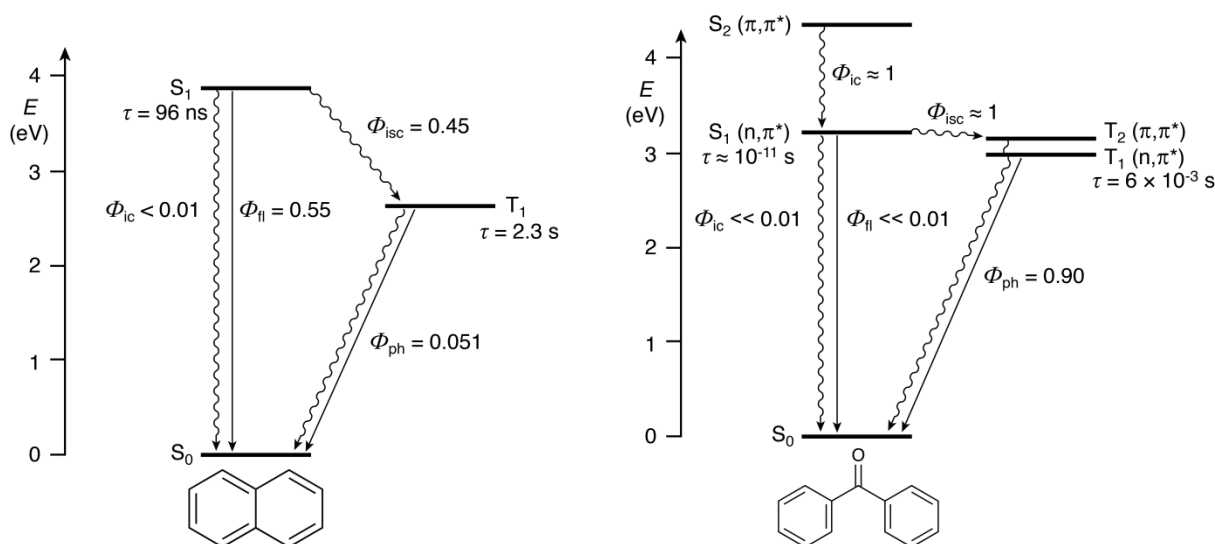
Phosphorescence quantum yield is the product of the efficiency of population of  $T_1$  ( $\eta_{isc}$ ) by upper lying excited states ( $S_1$  in the example reported in Figure 1 and equation 4) and the intrinsic efficiency of phosphorescence ( $\eta_{ph}$ ), i.e. the percentage of  $T_1$  deactivating by phosphorescence. Since we are interested in bright and long-lived phosphorescent organic molecules, we will discuss the parameters affecting  $\Phi_{ph}$  and  $\tau(T_1)$ , bearing in mind that we need to maximize both the efficiency of isc ( $\eta_{isc}$ ) and the efficiency of phosphorescence ( $\eta_{ph}$ ).

When the molecule contains heavy atoms, the formally forbidden intersystem crossing and phosphorescence processes become faster. The spin selection rules of radiative and non-radiative processes are valid to the extent to which spin and orbital function can be separated rigorously. Departures from this approximation are due to spin-orbit coupling, which mix electronic states of different multiplicity and increases as the atomic number of the atoms involved increases (for an atomic species, spin-orbit coupling is proportional to the fourth power of atomic number,  $Z^4$ ). This is the reason why most of the phosphorescent materials are based on metal complexes, but a similar heavy-atom effect is induced also by the presence, for example, of halogen atoms in the molecules (*internal* heavy-atom effect) or in the solvent or polymeric matrix (*external* heavy-atom effect). The heavy-atom effect is larger when the "heavy atom" is directly involved in the phosphorescence decay, meaning that the orbitals involved in the corresponding electronic transition are also localized on that atom, or it is interacting with an atom involved in the phosphorescence deactivation.<sup>1</sup>

The rate of non-radiative inter system crossing processes is increased also when (i) the involved singlet and triplet states belong to different electronic configurations, according to El-Sayed rules:<sup>26</sup> inter system crossing like  $^1(n,\pi^*) \rightarrow ^3(\pi, \pi^*)$  are substantially faster than those between states of the same orbital nature, e.g.  $^1(n,\pi^*) \rightarrow ^3(n, \pi^*)$ ; (ii) the energy difference between the involved electronic states is low because of a higher spin-orbit coupling and a better vibrational overlap of the initial and final states (energy gap law).<sup>23</sup> The energy separation between the singlet and triplet states of a given electronic configuration arises from the repulsion experienced by neighboring electrons and corresponds to twice the electron exchange integral.<sup>23,24</sup> When the electronic transition is  $(n, \pi^*)$ , the two orbitals barely overlap since they lie in orthogonal planes, so that the singlet-triplet splitting is small. The same holds true for electronic transition with charge-transfer character since the spatial orbital overlap is limited. On the other hand, the splitting of singlet-triplet states deriving from  $(\pi, \pi^*)$  transitions is relatively large since the orbital overlap is considerable.

With regard to lifetime of  $T_1$ , it is generally much shorter for  $^3(n, \pi^*)$  states than for  $^3(\pi, \pi^*)$  states. This experimental finding can be rationalized as follows: the nominal  $^3(\pi, \pi^*)$  state of ketones, for example, has a significant singlet character because of the efficient spin-orbit coupling with higher lying singlet states of different orbital nature, like  $^1(\pi, \pi^*)$ , and thus deactivation to the singlet ground state is relatively fast. On the other hand, for aromatic molecules, like naphthalene, all the lowest states have  $(\pi, \pi^*)$  character and spin-orbit coupling between states of the same orbital nature is very poor, according to El-Sayed rules, so that  $T_1$  can be regarded as a pure triplet state except in so far as vibronic spin-orbit coupling relaxes symmetry constraints.<sup>3</sup>

It is now worth considering two prototypical examples, i.e. naphthalene and benzophenone, to illustrate the concepts outlined above.



**Figure 2.** Schematic Jablonski diagram for naphthalene (a) and benzophenone (b) in rigid matrix at 77 K (solid line for emission processes and wavy lines for non-radiative processes).

Figure 2 reports the Jablonski diagrams of naphthalene and benzophenone at 77 K. It is worth noting that, as discussed above, the energy gap  $S_1$ - $T_1$  is much larger for  $(\pi, \pi^*)$  states of naphthalene than for  $(n, \pi^*)$  state of benzophenone and that the lifetime of the  $^3(\pi, \pi^*)$  state is much longer than that of  $^3(n, \pi^*)$  of benzophenone.

Naphthalene is poorly phosphorescent also in rigid matrix:  $\Phi_{ph} = 0.051$  and  $\tau(T_1) = 2.3$  s. Comparison of naphthalene with naphthalene carrying a halogen atom in position 1 demonstrates the heavy-atom effect on  $k(S_1 \rightarrow T_1)$  (Table 1). Indeed, the heavy-atom effect markedly increases the rates of both radiative and non-radiative singlet  $\leftrightarrow$  triplet processes, according to the following considerations and with references to the processes reported in Figure 1:

$$k_{isc}(S_1 \rightarrow T_1) \text{ increases} \Rightarrow \tau(S_1) \text{ and } \Phi_{fl} \text{ decrease, } \eta_{isc}(S_1 \rightarrow T_1) \text{ increases} \quad (5)$$

$$k'_{isc}(T_1 \rightarrow S_0) \text{ increases} \Rightarrow \tau(T_1) \text{ and } \eta_{ph} \text{ decrease} \quad (6)$$

$$k_{ph}(T_1 \rightarrow S_0) \text{ increases} \Rightarrow \tau(T_1) \text{ decreases and } \eta_{ph} \text{ increases} \quad (7)$$

Therefore, the heavy-atom effect brings about a decrease of  $\tau(S_1)$ ,  $\tau(T_1)$  and  $\Phi_{fl}$ , but it is difficult to predict if the phosphorescence quantum yield will increase or decrease as a result of the heavy-atom effect, for processes (5) and (7) conflict with process (6). For example, in the case of naphthalene derivatives  $\Phi_{ph}$  decreases going from 1-chloronaphthalene to 1-bromonaphthalene (Table 1).

**Table 1.** Internal heavy-atom effect on electronic transitions between states of naphthalene derivatives in rigid matrix at 77 K (vol. 2, p. 126 of ref. <sup>27</sup>)

Molecule	$\Phi_{fl}$	$\Phi_{ph}$	$\tau(T_1)$ (s)	$\eta_{isc}$	$k_{ph}$ ( $s^{-1}$ )	$k_{isc}$ ( $s^{-1}$ )	$k'_{isc}$ ( $s^{-1}$ )
Naphthalene	0.55	0.051	2.3	0.45	0.05	$0.82 \times 10^6$	0.39
1-Fluoronaphthalene	0.84	0.056	1.5	0.16	0.23	$0.57 \times 10^6$	0.42
1-Chloronaphthalene	0.058	0.30	0.29	0.94	1.10	$49 \times 10^6$	2.35
1-Bromonaphthalene	0.0026	0.27	0.02	1	13.5	$1850 \times 10^6$	36.5
1-Iodonaphthalene	<0.0005	0.38	0.002	1	190	$>6000 \times 10^6$	310

In the case of benzophenone, a very strong phosphorescence is observed at 77 K with  $\Phi_{ph} = 0.90$  and a lifetime of 6 ms. The phosphorescence quantum yield is so high thanks to the unitary efficiency of the population of  $T_1$  by  $S_1$ : such a remarkable value is possible since the  $S_1(n, \pi^*)$  deactivation does not lead directly to the  $T_1(n, \pi^*)$  state, which would be a forbidden process according to El-Sayed rules, but to the  $T_2(\pi, \pi^*)$ , which is an allowed process. Then,  $T_2(\pi, \pi^*)$  relaxes rapidly to the very close  $T_1(n, \pi^*)$  state by internal conversion.

Another example of a carbonyl compound exhibiting phosphorescence is biacetyl, strongly phosphorescent in solid, solution and gas phase.<sup>1,28</sup>

Up to now, we discussed deactivation of excited states only by intrinsic (first order) decay channels (Figure 1), but it can occur also by interaction with other species (called “quenchers”) following second order kinetics. The kinetics of the quenching process is described by the Stern-Volmer equation in fluid solution:

$$\tau^0/\tau = \Phi^0/\Phi = 1 + k_q \tau^0 [Q] \quad (8)$$

where  $\tau^0$  and  $\tau$  (or  $\Phi^0$  and  $\Phi$ ) are the lifetimes (or emission quantum yields) of the chromophore in the absence and presence of the quencher, respectively,  $k_q$  is the quenching constant and  $[Q]$  is the molar concentration of the quencher.

In the case of phosphorescence, a typical quencher is dioxygen that is usually dissolved at mM concentrations in air-equilibrated solvents.<sup>29</sup> From equation 8, you can estimate that for a chromophore with  $\tau^0(T_1)=1$  ms,  $[Q] = 1$  mM and  $k_q=10^9$  M<sup>-1</sup> s<sup>-1</sup>, the resulting phosphorescence quantum yield is 1000 times lower than  $\Phi^0$ . This is the reason why spectra of long-lived phosphorescent organic molecules are usually recorded in rigid matrix at 77K to prevent quenching by diffusing quenchers, like dioxygen or other impurities present in the solvent. On the other hand, the effect of the temperature on  $k_{ph}$  is quite limited. In the case of  $S_1$  excited states, which have much shorter lifetimes, bimolecular quenching processes are not effective, unless very high concentrations of quenchers are employed. Provided the solution are very thoroughly deoxygenated, it is possible to observe phosphorescence in fluid solutions of low viscosity at room temperature, but the  $T_1$  lifetime is much shorter than in rigid glass at 77 K and correspondingly the phosphorescence quantum yield is much lower. For example, benzophenone exhibits a lifetime of 6.9  $\mu$ s at 298 K and 6 ms at 77K.<sup>29</sup> The discrepancy is mainly due to the quenching by impurities: for lifetime of the order of a few seconds, quenching can occur when impurity concentration is as low as 10<sup>-8</sup> M.

Another second order process that deactivates  $T_1$  is observed when the  $T_1$  concentration is high, like in concentrated solution of chromophores displaying long-lived  $T_1$  excited states or in pure organic crystals; it is named triplet-triplet annihilation:



This process was first evidenced by observing delayed fluorescence of pyrene,<sup>30</sup> i.e. fluorescence due to the radiative deactivation of  $S_1$  produced according to equation 9. It is usually an exergonic process since the energy gap between  $T_1$  and  $S_0$  is generally larger than that between  $S_1$  and  $T_1$  (see Figure 1 as a representative case). This process was studied in the past in pure crystals of naphthalene and benzophenone, where triplet excited states can migrate among neighboring molecules and finally annihilate or be quenched by impurities. Triplet-triplet annihilation was observed to be predominant in naphthalene crystals rather than in benzophenone crystals because of the different orbital nature and much longer lifetime of naphthalene  $^3(\pi, \pi^*)$  state compared to benzophenone  $^3(n, \pi^*)$  state.<sup>31,32</sup>

Based on the above-reported discussion, design of organic molecules displaying long-lived and highly intense room-temperature phosphorescence is a difficult task. For example, molecules possessing  $T_1$  excited state with a charge-transfer character, i.e.  $(n, \pi^*)$  transitions, usually display bright phosphorescence with short-lifetime. On the other hand, aromatic molecules like naphthalene and pyrene with  $^3(\pi, \pi^*)$  excited state are usually weakly phosphorescent, but with a long lifetime. Indeed, a long  $T_1$  lifetime means that  $T_1$  is subject to quenching by a very low-concentration of impurities even in the crystals thanks to triplet energy migration, so that complete exclusion of dioxygen and very pure samples are needed in order to observe room-temperature phosphorescence. It is worth noting that long-lived phosphorescence (ms to s) is not desirable for all applications. For example, in the case of OLEDs, phosphorescent chromophores with long lifetimes are detrimental since they bring about a decrease of the overall efficiency.<sup>33</sup>



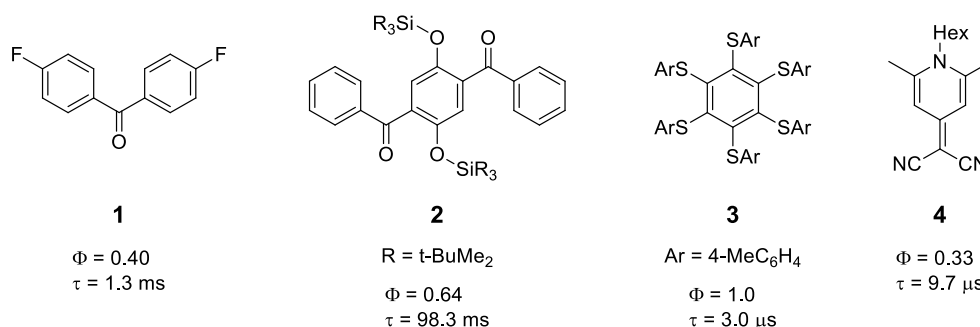
In the following, we will discuss the most recent results with particular emphasis on the most instructive examples, divided into two main classes in which phosphorescence is switched on by: (i) rigidification of the matrix (in a crystal or polymeric matrix) or (ii) interaction with other molecules of the same type (H-aggregation) or different type (heavy-atom effect).

## 1. Rigidification-induced phosphorescence

Reducing the mobility (e.g., rotation) of a chromophore is one of the most explored and effective strategies to increment the phosphorescence quantum yield by diminishing the impact of quenching and non-radiative processes. In the following, we refer to *rigidification-induced phosphorescence* when the reduced mobility is due to non-bonding interactions with the “environment” surrounding the chromophore. By far the most explored implementation of this strategy is represented by inclusion of the chromophores in a rigid crystalline lattice. To succeed in this approach the compound has to be chemically engineered, mostly in a trial and error way, to make it a crystallization synthon. Alternatively, embedding the luminophore in a rigid polymeric host matrix is another widely explored strategy to reduce their mobility and promote room temperature solid state phosphorescence. This last strategy, while less heuristic in its approach, puts narrow constraints on the nature of the employed polymeric matrix mainly due to the necessity of being light transparent and chemically compatible with the luminophore.

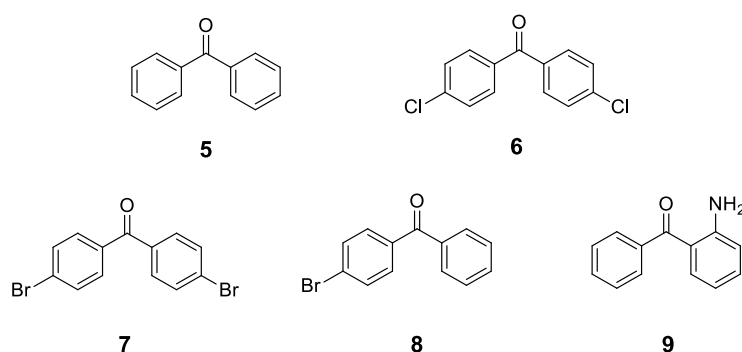
### 1.1 Rigidification induced by crystallization

Crystallization represents a rational strategy, highly explored in the literature, to develop persistent room temperature phosphorescent organic materials. However, the reported phosphorescence quantum yields of most metal-free organic crystals are generally rather low:  $\Phi_{ph} < 0.3$ . Exceptions are limited to single crystals of 4,4'-difluorobenzophenone (**1**),<sup>34</sup> 1,4-dibenzoyl-2,5-bis(siloxy)-benzenes (**2**),<sup>35</sup> 1,2,3,4,5,6-hexakis(arylthio)benzenes (**3**),<sup>36,37</sup> and 2-(1-hexyl-2,6-di-methylpyridin-4H-ylidene)malononitrile (**4**)<sup>38</sup> (Figure 3). Therefore, the design of metal-free chromophores with high quantum yields at ambient conditions remains a formidable challenge mostly due to the trial and error nature intrinsic to the stringent requirements of preparing high quality crystalline materials.



**Figure 3.** Chemical structures of high quantum yield solid state crystalline phosphorescent molecules. Phosphorescence quantum yield ( $\Phi$ ) and lifetime of the lowest triplet excited state ( $\tau$ ) are reported for comparison.

The first examples of a crystal engineering approach to efficient organic phosphorescence is represented by simple pure organic chromophores, such as benzophenone and 4,4'-dibromobiphenyl.<sup>34</sup> Benzophenone and its derivatives containing halogen atoms **1**, **5-9** (Figure 4) are poorly emissive when dissolved in good solvents, adsorbed on TLC plates, or doped into polymer films, but display quite intense phosphorescence at room temperature upon crystal formation. The phenomenon is general for this class of materials and the long lifetime of the emitting excited states ( $\tau$  up to 4.8 ms) confirms the spin-forbidden nature of the radiative transition. The restriction of rotational motion due to multiple inter-molecular interactions induced by physical confinement in the crystalline lattice is mainly responsible for the enhancement of the phosphorescence in the solid state.

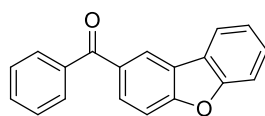


**Figure 4.** Chemical structures of benzophenone derivatives displaying crystallization induced phosphorescence.<sup>34</sup>

That the interplay between non-bonding interactions in the solid state molecular arrangement is critical for the observation of solid state phosphorescence is elegantly evidenced in the study of crystalline compound **2** (Figure 3). It exhibits solid-state phosphorescence with excellent quantum yield and long lifetime, as reported in Figure 3. Comparison between the corresponding bis(trimethylsilyl)- and bis(silylmethyl)-substituted benzenes revealed that the siloxy group is essential for the excellent luminescent performance.<sup>39</sup> In the crystalline structure, the hydrogen bonds between the carbonyl oxygens and hydrogens of the tert-butyl group bonded to the silicon diminish intramolecular motion, slowing down the rate of non-radiative decay of the phosphorescent excited state. According to DFT calculations, excitation to  $S_1$  occurs via an  $n \rightarrow \pi^*$  transition from a silicon-attached oxygen atom to the carbonyl moieties. It is proposed that the remarkable luminescence performance of **2** is related to the stabilization of  $T_1$  by  $\sigma$ - $n$  conjugation between Si-C  $\sigma$ -orbital(s) and the half-vacant nonbonding orbital on the oxygen of the siloxy group. ESR experiments support the proposed generation of the paramagnetic triplet state. The efficient induction of phosphorescence by siloxy groups, whose effect is remarkably greater than that of bromine, is unique and is important for future development in the field.

Another benzophenone derivative displaying bright and long-lived phosphorescence is compound **10** (Figure 5): the crystalline powder displays a green phosphorescence with  $\Phi_{ph} = 0.35$  and  $\tau(T_1) = 0.2$  s, while no emission is recorded in solution or amorphous powder, unless the sample is cooled down to 77K.<sup>40</sup> The authors examined a series of these benzophenone compounds featuring aromatic moieties to investigate the spin-orbit coupling constant and its correlation with the  $(n, \pi^*)$  character of the involved excited states in the series. The excellent performance of compound **10** is related to the presence of a  $T_2$  state with a strong  $(n, \pi^*)$  character, located slightly lower than the  $S_1$  excited state populated by light excitation. This assures a

strong spin-orbit coupling, which promotes an efficient inter system crossing.  $T_2$  rapidly deactivates, by internal conversion, to  $T_1$ , which displays a strong ( $\pi, \pi^*$ ) character and thus a much longer lifetime compared to the archetypal benzophenone.



**10**

$$\Phi = 0.35$$

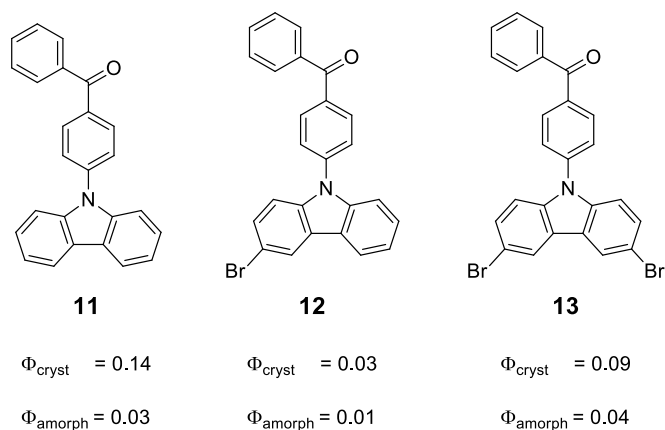
$$\tau = 0.2 \text{ s}$$

**Figure 5.** Chemical structure and photophysical properties of a benzophenone derivative.<sup>40</sup>

Compound **3** (Figure 3) is based on a hexathiobenzene core and it exhibits no luminescence in fluid solution and a very intense green phosphorescence when the molecule experiences a rigid environment (*i.e.* in a frozen solution at low temperature or in the crystalline state):<sup>36</sup> an emission quantum yield of 1.0 was reported for the crystalline state. This is a consequence of a decrease of intramolecular rotations and motions; conformational and rotamer issues along with substituent effects might also play a role. A detailed computational study disclosed an important role of CH –  $\pi$  interactions: indeed, the analog of molecule **3** featuring six isopropyl groups instead of six tolyl groups attached to the sulfur atoms is not luminescent also in rigid matrix because of a different nature of the lowest triplet excited state showing a very efficient non-radiative inter system crossing to the singlet ground state. Compound **3** has been exploited in luminescent organic nanocrystals and light-emitting diodes with a fully solution processable technology. In order to rationalize the optical properties as a function of the chemical structure, a series of functionalized persulfurated benzene molecules were analyzed from the point of view of optical properties and crystal packing.<sup>37</sup> All compounds exhibit very similar optical properties in terms of the energy of  $S_1$  and  $T_1$  excited states: they are non-emitting in solution at room temperature and phosphorescent in the solid state at room temperature with emission quantum yields ranging from 0.06 to 1.0. The authors suggest that the restriction of molecular rotations and motions is the most important factor for observing phosphorescence enhancement, but a conformational issue can also be responsible for the differences observed in the phosphorescence emission quantum yields in a rigid environment.

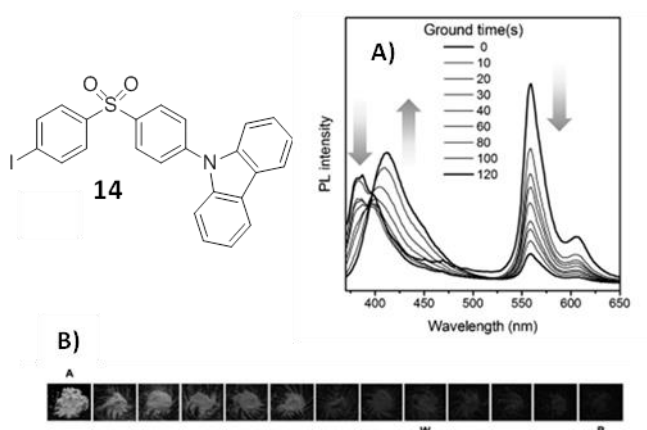
Recently, it was proven that even simple aromatic hydrocarbons in the form of aggregated hydrosol of benz(a)anthracene show crystallization induced phosphorescence emission at room temperature.<sup>41</sup> The crystalline microstructures obtained by re-precipitation of benz(a)anthracene using sodium dodecyl sulfate as soft template display a long lived (ms timescale) red emission. Theoretical calculations suggest that restriction of intermolecular motion induced by molecular packing is again responsible of locking the molecular conformation, thus hindering non-radiative deactivation pathways.

It is important to appreciate that in all these classes of materials, where phosphorescence is induced by the solid state arrangement, any perturbation able to alter the crystalline lattice can cause changes in the luminescence properties allowing the development of “smart” mechanosensitive materials. This possibility is exploited in a set of carbazole-benzophenone based molecules (compounds **11-13** in Figure 6) with a donor-acceptor structure.<sup>42</sup> These compounds exhibit long-lived solid state phosphorescence with  $\tau$  up to 520 ms. All of these chromophores display a reversible mechanochromism between crystalline and amorphous states, accompanying the presence and disappearance of triplet emissions.



**Figure 6.** Chemical structure and corresponding photophysical property of carbazole-benzophenone based molecules.  $\Phi_{\text{cryst}}$  and  $\Phi_{\text{amorph}}$  represent phosphorescence quantum yields in the crystalline and amorphous phase, respectively.<sup>42</sup>

Simultaneous fluorescence and phosphorescence in a single pure organic compound at ambient conditions is unusual. This rare property has been applied to obtain a mechanosensitive solid-state emission color tuning in donor-acceptor type diphenylsulfone derivatives. In particular, 4-iodo-4'-(N-carbazolyl)diphenylsulfone (compound **14** in Figure 7) displays a strong solid-state emission composed by the superposition of a very strong fluorescence peak together with a weak phosphorescence peak separated by over 150 nm in the crystalline state in air. Mechanical grinding of the crystals leads to an amorphous powder, which exhibits an unusually wide range of blue shift in its emission: color changes from orange to purple due to the disruption of the crystalline lattice that affects phosphorescence and not fluorescence.<sup>43,44</sup> Similar results have been obtained for another carbazole derivative, namely 4-(carbazol-9-yl)benzaldehyde, which exhibits reversible conversion from phosphorescence to fluorescence by grinding.<sup>45</sup>



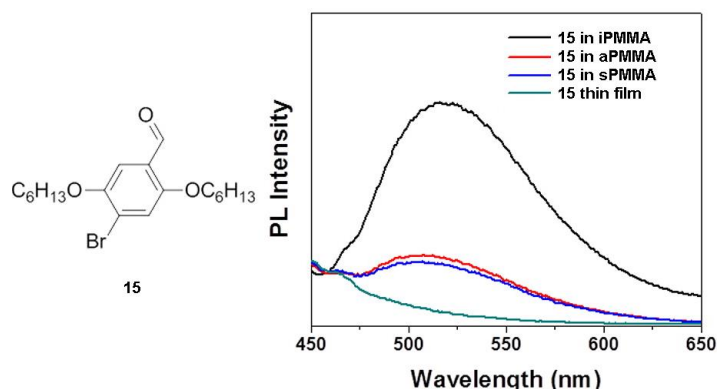
**Figure 7.** Chemical structure of donor-acceptor type diphenylsulfone derivative **14** and (A) photoluminescence (PL) spectra of **14** at different grinding times. Excitation wavelength: 350 nm. (B) Corresponding photos of the samples of **14** at different grinding time under 365 nm UV irradiation.<sup>43</sup> Copyright © 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Adapted by permission of John Wiley & Sons, Inc.

Crystallization-induced phosphorescence has been reported also for triphenylphosphine chromophores with a 27-time increase of the phosphorescence quantum yield going from solution to crystals ( $\Phi = 26.8\%$ ).<sup>46</sup>

### 1.2 Rigidification induced by encapsulation in a polymer matrix

Embedding molecules in the rigid environment of a polymeric matrix is another valuable strategy to inhibit vibrational relaxation and quenching by impurities. This is, at least in principle, a more general approach to inhibit non-radiative pathways compared to rigidification through molecular engineering of highly crystalline chromophores that has proved to be highly successful, but intrinsically heuristic in nature.

Bright room temperature phosphorescence has been achieved by embedding purely organic phosphors into amorphous glassy polymer matrix (Figure 8). The tacticity of PMMA strongly affects quantum efficiency of the embedded organic phosphors: isotactic PMMA most efficiently suppresses the non-radiative triplet decay and allows the embedded organic chromophore to achieve high phosphorescence quantum yield.<sup>47</sup> This system can also be used as a temperature sensor: phosphorescence intensity becomes highly sensitive to temperature by embedding the compound into a temperature-sensitive matrix, such as PMMA with a low glass transition temperature.

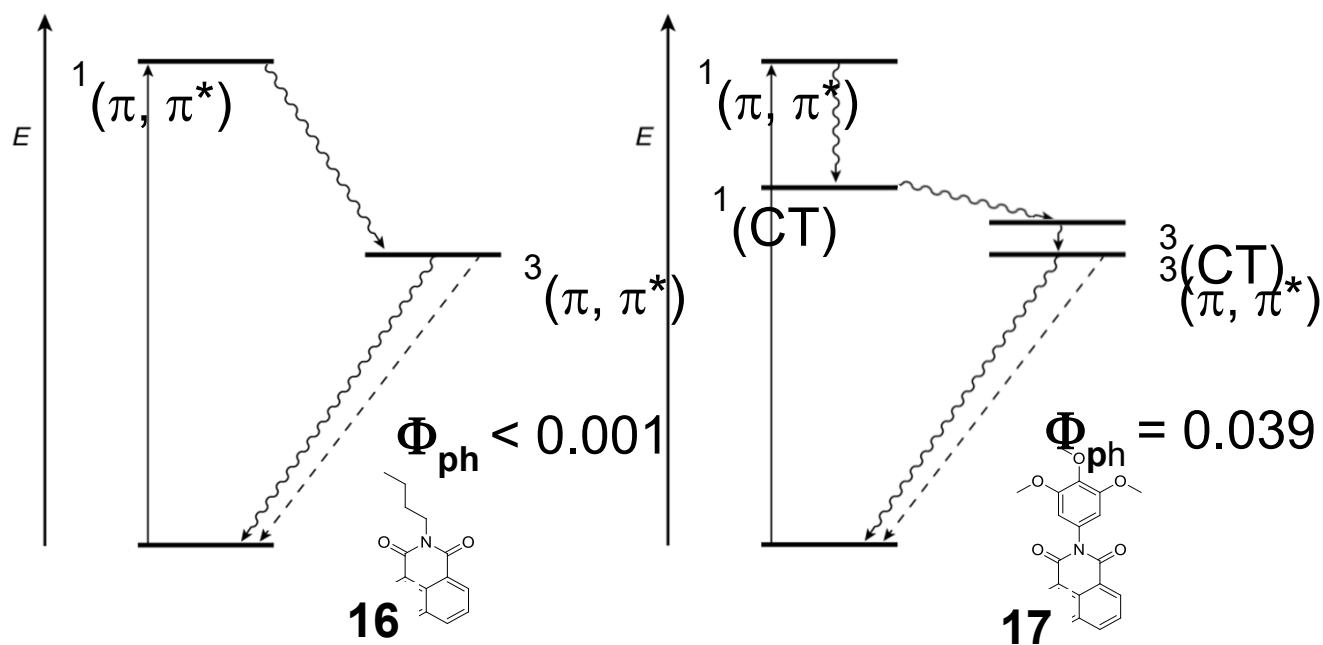


**Figure 8.** Chemical structure of the phosphor **15** and photoluminescence (PL) spectra of **15** in thin film and embedded in isotactic PMMA (iPMMA), atactic PMMA (aPMMA) and syndiotactic PMMA (sPMMA).  $\lambda_{\text{ex}} = 365$  nm.<sup>47</sup> Adapted with permission from reference 47. Copyright 2013 American Chemical Society.

Cross-linking between the chromophoric unit reported in Figure 8 and polymer matrices via Diels–Alder click chemistry results in a sharp increase in phosphorescence quantum efficiency: ca. two to five times higher than that of phosphor-doped polymer systems having no such covalent linkage.<sup>48</sup> This strategy is a new and versatile method to restrict molecular motion and induce room temperature phosphorescence.

The design principle described for compound **10** has been used, in a similar way, to switch on the phosphorescence of naphthalimide derivatives in PMMA films.<sup>49</sup> Naphthalimide chromophore **16** shows very weak phosphorescence in PMMA films, a result that can be rationalized on the basis of the schematic Jablonski diagram shown in Figure 9. The lowest singlet and triplet excited states are separated by a large energy difference, as expected for ( $\pi, \pi^*$ ) transition (see above). The large energy difference brings about a low spin-orbit coupling, so that population of the  $T_1$  state is inefficient. Compound **17** carries a

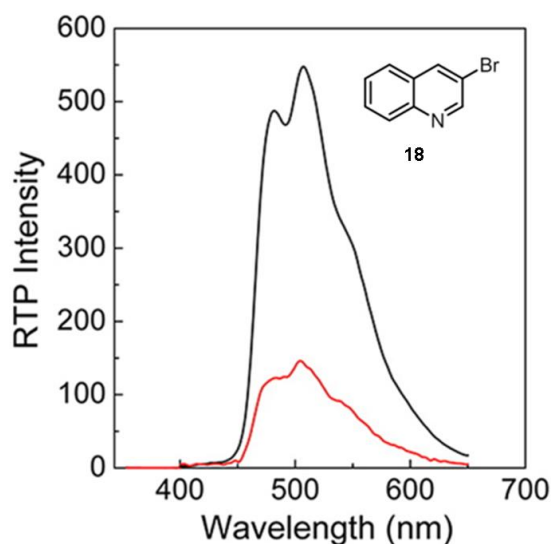
trimethoxyphenyl substituent on the imide nitrogen, which introduces a charge-transfer transition, characterized by a much smaller singlet-triplet energy splitting. As reported in Figure 9, fast inter system crossing between  $^1\text{CT}$  and  $^3\text{CT}$  is expected, which then results in the efficient population of the lowest  $^3(\pi, \pi^*)$  state by internal conversion. Moreover, encapsulation of the naphthalimide chromophore **17** in PMMA film switch on the phosphorescence characterized by  $\Phi=0.039$  and  $\tau=0.23$  s.



**Figure 9.** Chemical structure of naphthalimide chromophores **16** and **17**<sup>49</sup> and the corresponding Jablonski diagram showing the most relevant photophysical processes (solid line for absorption, dashed line for emission processes and wavy lines for non-radiative processes).

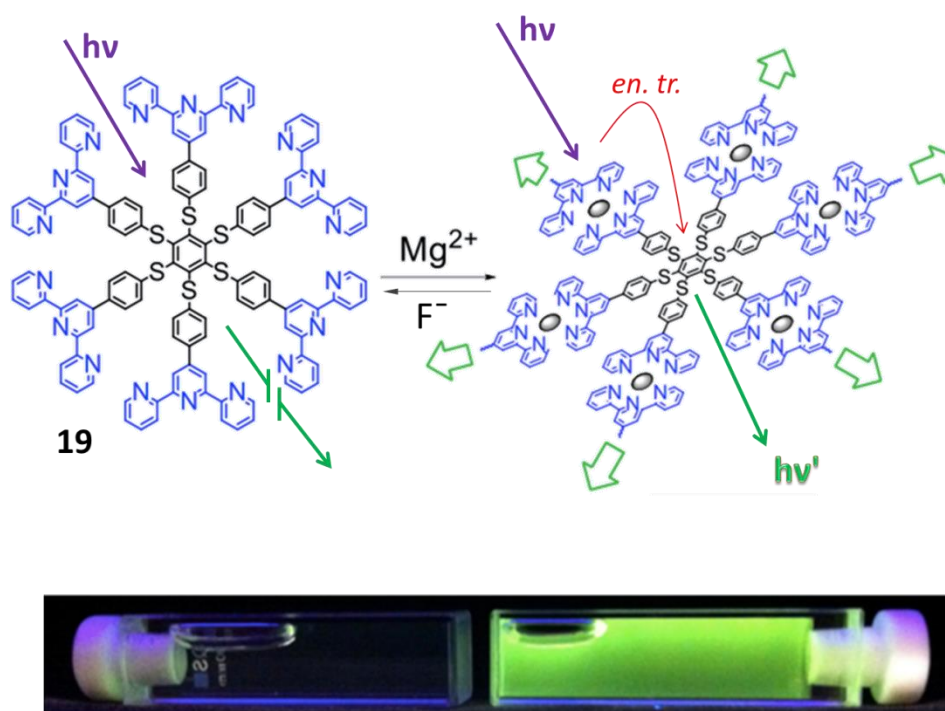
Amorphous rigid steroidal compounds have also been applied to minimize quenching of long-lived triplet excited states and achieve efficient and persistent phosphorescence in pure organic amorphous guest materials in air.<sup>50–52</sup> This type of host-guest systems enabled the fabrication of afterglow OLEDs by introducing an organic aromatic phosphorescent emitter layer into an OLED structure.<sup>53</sup>

Beside rigid polymeric matrices, gels represent a flexible and highly tunable matrix ideal to control the environment of luminophores. Thermally on–off reversible room temperature phosphorescence has been achieved by entrapping 3-bromoquinoline (**18** in Figure 10) into supramolecular gels formed by the self-assembly of sorbitol derivatives.<sup>54</sup> The gel state exhibits strong phosphorescence. The chromophore is entrapped in the hydrophobic 3D network structure of gels, thereby restricting the motion of **18** and avoiding the quenching of its phosphorescence.



**Figure 10.** Room temperature phosphorescence (RTP) spectra of 3-bromoquinoline **18** in a gel (black curve) and sodium deoxycholate solution (red curve).<sup>54</sup> Adapted with permission from reference 54. Copyright 2015 American Chemical Society.

Compound **19** (Figure 11) represents a peculiar case of room temperature phosphorescence triggered by encapsulation in a polymer matrix.<sup>55</sup> It contains the previously discussed hexathiobenzene chromophore **3**, which is not phosphorescent in fluid solution and becomes highly phosphorescent upon crystallization or rigidification of the matrix, appended with six terpyridine ligands at its periphery. The absorption spectrum shows no ground-state interaction between the central chromophore and the terpyridine ligands. No luminescence is observed in fluid solution upon excitation of either the core or the peripheral terpyridine ligands, while phosphorescence ( $\Phi=0.02$ ,  $\tau=1.7$ ,  $11.6\ \mu\text{s}$ ) is observed in the solid state. Upon titration of **19** in air-equilibrated THF solution with  $\text{Mg}(\text{ClO}_4)_2$  salt, a red-shifted absorption band appears and reaches its maximum intensity upon addition of three metal ions per molecule. Concomitantly, a phosphorescence band with maximum at 545 nm, very similar to that observed for the solid sample of **19**, increases up to the addition of 3 equivalents of metal ions reaching a phosphorescence quantum yield of 0.10. These results are rationalized by the formation of a supramolecular polymer (Figure 11), as confirmed by DLS and AFM analysis: nanoparticles with a diameter of approximately 60 nm are formed. This structure inhibits intramolecular rotations and motions, thus favouring radiative deactivation. The supramolecular polymer can be disassembled upon fluoride addition, thus switching off the luminescence. Moreover, it performs as a light-harvesting antenna: excitation of the  $[\text{Mg}(\text{tpy})_2]^{2+}$  units sensitizes the hexathiobenzene core luminescence with almost unitary efficiency. The novelty of the present system is that metal ion coordination is not directly involved in the phosphorescence process; it induces the formation of a supramolecular polymer displaying *phosphorescence* in air equilibrated solution, *light-harvesting* abilities and *sensing* properties. Indeed, the present system is a sensor of both metal cations and fluoride anions.



**Figure 11.** Chemical formula of compound **19**, that is not emissive in fluid solution, and the polymeric structure reversibly formed upon Mg(II) complexation. A picture of the corresponding solutions under UV light excitation is reported at the bottom.<sup>55</sup> Adapted with permission from reference 55. Copyright 2014 American Chemical Society.

## 2. Interaction-induced phosphorescence

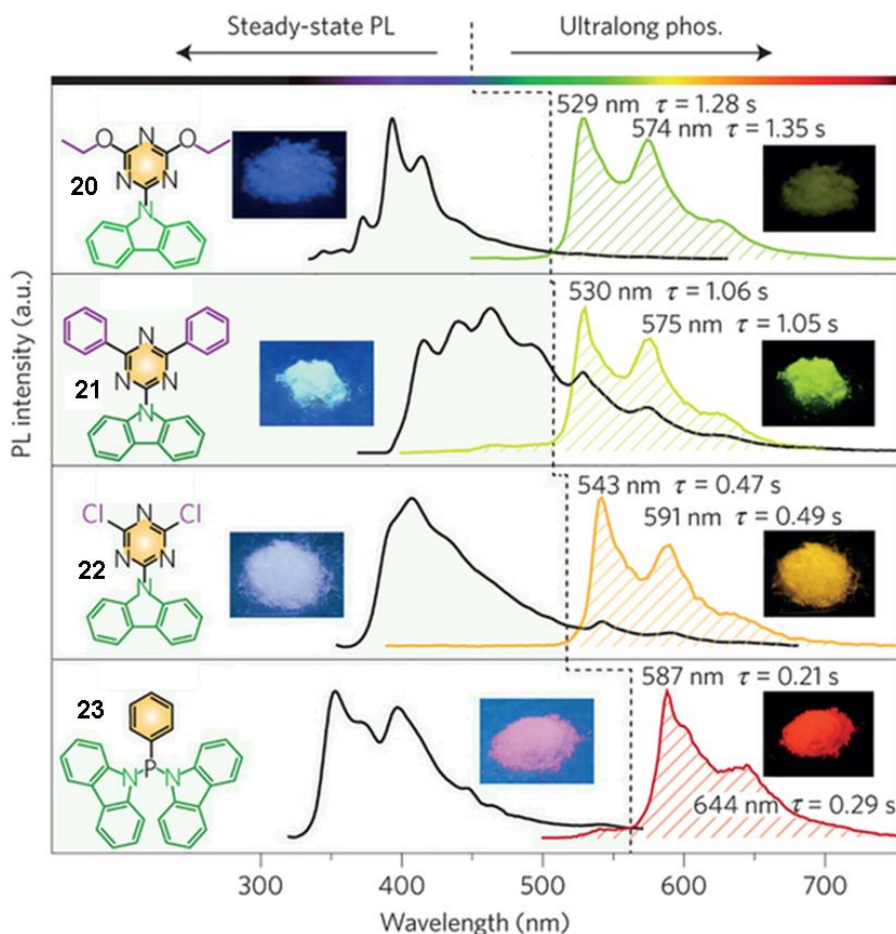
Electronic interactions among chromophores or between a chromophore and the surrounding matrix is a viable route to access intense and long-lived phosphorescence by: (i) the formation of lower lying excited state compared to the isolated chromophore or (ii) increase in the population of the phosphorescent excited state by spin-orbit coupling. Both of these approaches will be presented in the following.

### 2.1 Interaction among chromophores

Electronic interactions among chromophores favored by the close proximity and ordered array in solid state can lead to long-lived phosphorescence from organic molecules. A successful implementation of this approach is represented by a class of compounds based on carbazolyl-1,3,5-triazine (compounds **20-23** in Figure 12): the presence of aromatic units and O, N and P heteroatoms in their structure favors  $n, \pi^*$  electronic transition and hence facilitates the inter system crossing processes to populate the lowest triplet excited state.<sup>56</sup> Upon UV excitation at 365 nm, these compounds show an intense blue emission, which is the superposition of fluorescence and phosphorescence bands, in the solid state. By switching off the UV excitation source, the fluorescence disappears and remarkably long phosphorescence is registered at wavelengths over 500 nm with a lifetime of ca. 1.0 s and emission quantum yield of 0.01. By changing the



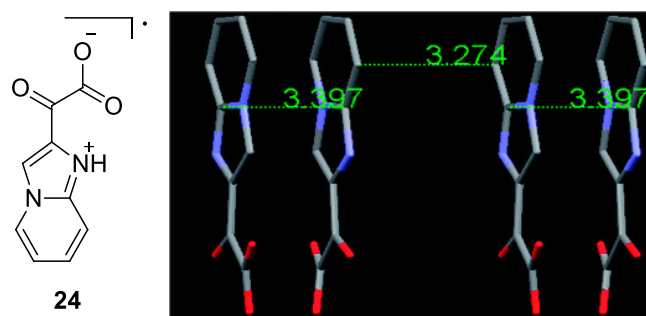
molecular structure, as reported in Figure 12, the color of the ultra-long phosphorescence can be tuned from green (515 nm) to red (644 nm) under ambient conditions. These results were tentatively rationalized on the basis of a stabilization of the triplet excited state of the chromophore by the formation of H-aggregates, compatible with the chromophore arrangement observed in the X-ray diffraction pattern of single crystals and computational calculations.



**Figure 12.** The steady-state photoluminescence (PL, left) and ultra-long phosphorescence (right) spectra of a series of carbazoyl-1,3,5-triazine molecules. Insets show the corresponding photographs taken before (left) and after (right) the excitation source is turned off. Excitation wavelength 365 nm at 300 K.<sup>56</sup> Adapted with permission from reference 56. Copyright © 2015, Rights Managed by Nature Publishing Group.

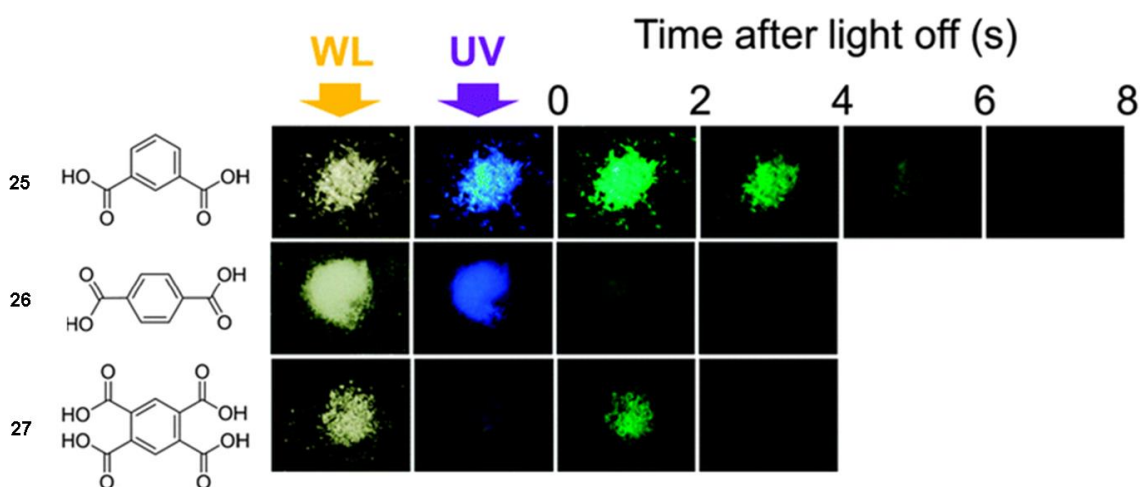
Stable organic radicals, namely 2-(imidazo [1,2-a]pyridin-2-yl)-2-oxoacetic acid (**24** in Figure 13), containing aromatic carbonyl group, exhibit interesting phosphorescence behaviour.<sup>57</sup> Compound **24** displays UV phosphorescence (no emission maximum at wavelengths longer than 380 nm) in aqueous solution and white phosphorescence in the solid state with emission maximum at 483 nm ( $\Phi_{ph} = 0.052$  and lifetime of ca. 20  $\mu$ s). In the solid crystalline state, it forms one-dimensional (1D) columnar chains, in which the molecules adopt slipped anti-parallel stacking modes. Although the stacking distance is outside van der Waals contact, there exist intermolecular close contacts in the crystal structure between neighboring molecules that might be responsible for intermolecular charge transfer interactions, leading to broad and lower energy phosphorescence bands compared to those observed in solution. The color can be tuned: the sodium salt of

compound **24** exhibits blue phosphorescence. Although information on the crystal structures is not present for the sodium salt, the change in emission color is expected to be related to a different crystal packing.

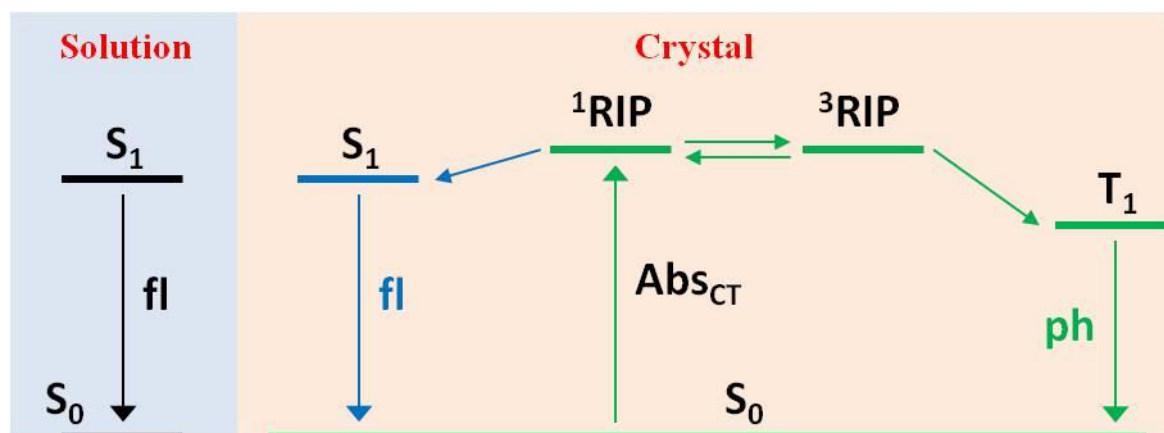


**Figure 13.** Formula and stacking interaction in the crystalline carboxylic acid radical 2-(imidazo[1,2-*a*]pyridin-2-yl)-2-oxoacetic acid **24**.<sup>57</sup> Adapted with permission from reference 57. Copyright © 2011, Royal Society of Chemistry.

Crystalline isophthalic acid (**25** in Figure 14) and analogous benzoic acids are another class of luminophore that exhibits room-temperature phosphorescence with an afterglow that lasts several seconds.<sup>58</sup> The phosphorescence mechanism of **25** is attributed to the forced packing of molecules that enables dimer formation leading to charge transfer (CT) absorption and radical ion pair (RIP) formation. Since separated radical pairs derived from CT has two electron spins over two molecules, the electron spins are only weakly coupled and thus the difference in energy between singlet (<sup>1</sup>RIP) and triplet (<sup>3</sup>RIP) excited states of radical ion pairs is so low that inter system crossing is highly favored and finally leads to the population of the T<sub>1</sub> excited state of the benzoic acid monomer, as schematically reported in Figure 15. The authors examine the effect of a magnetic field and report that stronger phosphorescence intensity is observed in the presence of a magnetic field. Moreover, as usual, the suppression of vibronic motions in the crystal favors phosphorescence compared to non-radiative decay of T<sub>1</sub> excited state. Delayed fluorescence by triplet-triplet annihilation (eq. 9) was also reported by the same authors. The phosphorescent afterglow facilitates a time-resolved detection and such phosphorescent materials are promising candidates in bioimaging applications.



**Figure 14.** Phosphorescence of crystalline benzoic acid derivatives on irradiation with white light (WL) or at 365 nm (UV) for isophthalic acid (**25**), terephthalic acid (**26**), and pyromellitic acid (**27**).<sup>58</sup> Adapted with permission from reference 58. Published by the PCCP Owner Societies.



**Figure 15.** Schematic energy level diagram showing the most important photophysical processes occurring for isophthalic acid **25** in solution and in crystals.<sup>58</sup> Adapted with permission from reference 58. Published by the PCCP Owner Societies.

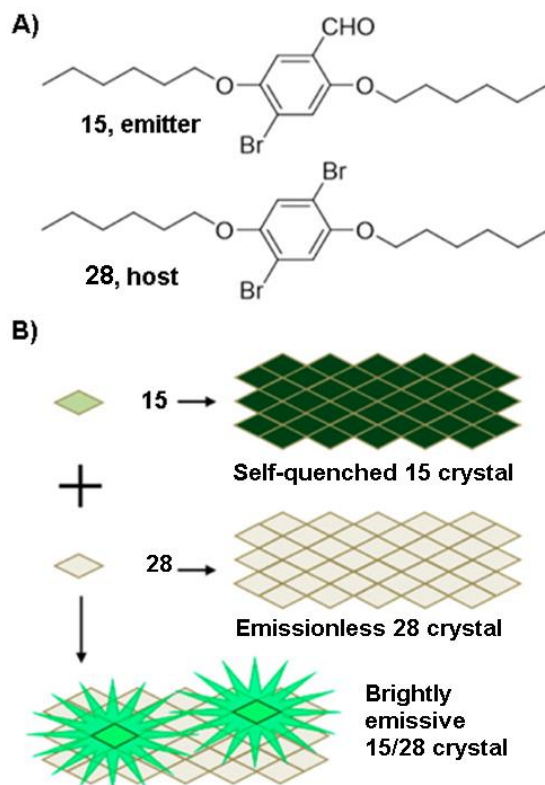
Both delayed fluorescence and persistent phosphorescence ( $\tau > 290$  ms) from isophthalic acid crystals was reported at ambient conditions.<sup>59</sup>

## 2.2 Interaction between the chromophore and the matrix

Beside reduction of vibrational deactivation pathways and quenching by dioxygen a matrix surrounding a luminophore can have a direct electronic effect on the guest molecule, thus affecting the excited state dynamics of the guest-molecules. The most effective realization of this concept utilizes a heavy halogen atom in the matrix embedding the luminophores to further increase the intersystem crossing rate of the coupled units. In order to fully take advantage of this effect, the heavy atom should be as close as possible to the molecular moiety where the triplet is produced. Therefore, in the case of carbonyl compounds, the heavy atom should be “bound” to carbonyl oxygen. The tendency of halogen atoms to interact with aromatic carbonyls (halogen bonding)<sup>60</sup> can thus be exploited.

The first example of this approach is represented by 2,5-dihexyloxy-4-bromobenzaldehyde **15** that exhibits a green phosphorescence at 500 nm, with a quantum yield 0.029 and a lifetime of 5.4 ms when excited at 360 nm in its crystal form.<sup>61</sup> Single-crystal X-ray diffraction (XRD) revealed that in the crystal of **15** there is an extremely close contact between the carbonyl oxygen and the bromine of the neighboring molecule. The C=O...Br angle of 126° falls within the range of reported halogen bonds and the distance 2.86 Å is among the shortest bromine–oxygen halogen bonds ever reported,<sup>60,62</sup> thus producing a very efficient heavy atom effect. However, **15** suffers greatly from self-quenching and to improve its performance, **15** needs to be diluted in the solid state, but it also needs to maintain its halogen-bonding motif that assures strong heavy atom effect on the carbonyl moiety. This result has been achieved by using 2,5-dihexyloxy-1,4-dibromobenzene (**28**, Figure 16), a bi-halogenated analogue to **15** with a second bromine in place of its

aldehyde group. The crystals made of **28** do not exhibit phosphorescence and XRD investigation revealed a halogen–halogen interaction very similar to the halogen bonding seen in crystals of **15**. XRD analysis of **15/28** mixed crystals containing ~10 wt% **15** revealed a unit cell identical to that of pure **15** crystals. The resulting mixed crystals (0.001 to ~1 wt% **15**) exhibit green phosphorescence very similar to the phosphorescent portion of the spectrum from pure **15** crystals, but with a much higher quantum yield (up to 0.5,  $\tau = 8.3$  ms).

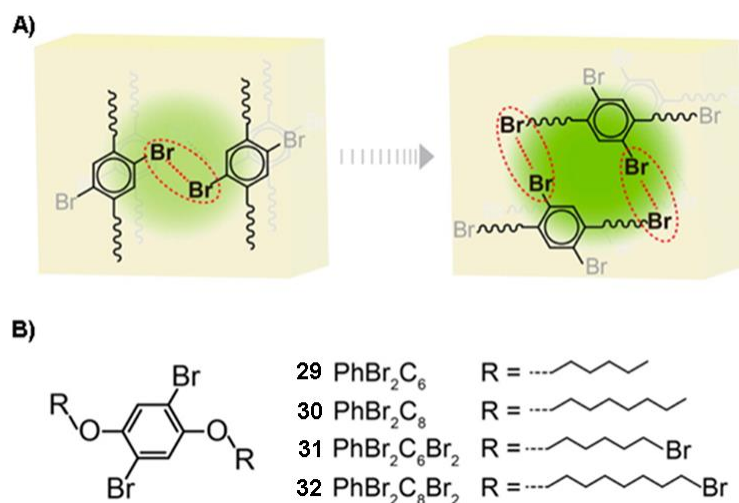


**Figure 16.** Bromobenzaldehyde purely organic phosphorescent crystals. (A) Benchmark aldehyde emitter and host, **15** and **28**, respectively. (B) Schematic illustration of **15** (emitter) crystals, non-emissive **28** (host) crystals, and bright phosphorescent **15/28** (mixed crystals).<sup>63</sup>

Phosphorescence from the mixed crystals is polarized, indicating that guest molecules are ordered in the host crystal. While host compounds tolerate a surprising variety of emitter sizes, both oversized and undersized, maximum quantum efficiency is reached when emitters and hosts are identically sized and the former is present at 1–10 wt% of total solids. The optimum quantum efficiency for these systems appears, empirically, to be in the range of 0.45–0.55. To fine-tune emission color, altering the halogen substitution of the emitter molecule affords sequential 5–30 nm changes to emission maxima within the green region, without significantly affecting the structure of the mixed crystals.<sup>63</sup>

In a similar approach modification of alkyl terminal groups with bromine atoms of bromobenzene derivatives **29–32** (Figure 17) enhances the phosphorescence efficiency in the crystalline state by manipulating heavy-atom interaction, as depicted in Figure 17b.<sup>64</sup> Bright green phosphorescence is observed for all these dibromobenzene derivatives in the solid state under ambient conditions due to the heavy-atom effect. By comparing differently substituted compounds (Figure 17c), the ones with four bromine atoms showed higher

luminescence quantum yield than the ones with two bromines. From the single-crystal analysis, it is evident that the enhancement of phosphorescence results from increased intermolecular heavy-atom interaction in the crystals of the compounds with more bromine atoms. Despite these attractive qualities, the mixed crystal motif defining these materials is very much demanding in terms of crystal packing, chemical structure, and sample preparation.



**Figure 17.** (A) Proposed strategy of manipulating heavy-atom interaction in the solid state. (B) Chemical structures of dibromobenzene derivatives.<sup>64</sup>

## Conclusions

Up to the last decade, most of the investigated phosphorescent materials were based on metal complexes, widely used in OLEDs, sensors, and photoelectrochemical cells. Although phosphorescence of organic molecules was known since the '40s, only recently, organic phosphorescent materials have attracted an increasing attention from theoretical and applicative point of view. Indeed, organic phosphors offer the advantages of a higher processability, biocompatibility and synthetic flexibility which enable the modulation of optical, electronic and solubility properties.

The design principles of organic molecules displaying bright and long-lived phosphorescence are based on old and well-known concepts of photophysics, revisited for a new application: (i) prevention of dioxygen quenching by encapsulation of the chromophore in a matrix or as a crystal; (ii) reduction of non-radiative decay rates of the phosphorescent excited state by rigidification of the system; (iii) efficient population of the phosphorescent excited state by promoting spin-orbit coupling via intramolecular or intermolecular heavy-atom effects and via a reduction of the energy separation between excited states involved in the inter system crossing process.

Some interesting applications of these materials have already been reported and highlighted in the present review. The future is now to develop these potential applications from a laboratory test up to industrial level in a variety of fields, ranging from sensors to lighting and information encoding devices. A particularly stimulating field of research in which organic phosphors can outperform their metal-based counterparts is that of phosphorescent sensors of viscosity, temperature or specific analytes: upon binding to a proper phosphor, luminescence is switched on by restriction of molecular motion. This fascinating area of research

can have a strong impact in imaging of nanostructures and biological objects by taking advantage of time-gated detection on a long-time scale (from  $\mu\text{s}$  to  $\text{ms}$ ) which eliminates scattered light and autofluorescence of the sample by low-cost equipment.

**Acknowledgments.** We gratefully acknowledge the European Commission ERC Starting Grant (PhotoSi, 278912).

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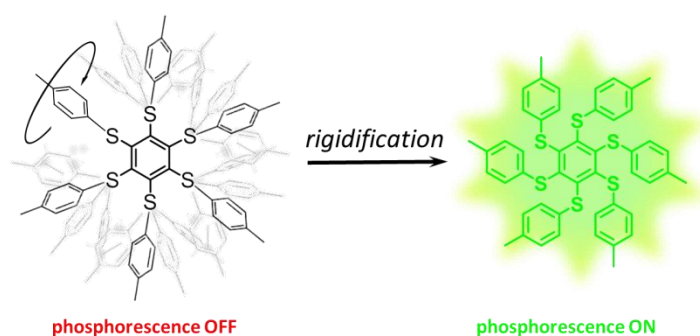
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## Table of Content



This feature article presents the principles and most recent examples of organic molecules in which long lived and highly intense room-temperature phosphorescence is switched on by rigidification of the matrix in a crystal or in a polymer or by interaction with other molecules.