Dibenzyl Isophthalates as Versatile Hosts in Room Temperature Phosphorescence Host-Guest Systems

Martin Molkenthin[a], Emanuel Hupf*[b] and Boris J. Nachtsheim*[a]

We report a series of dibenzyl isophthalates (DBIs) as versatile hosts for room-temperature phosphorescence (RTP) systems, leading to host-guest systems with quantum yields (QY) of up to 77 % or lifetimes of up to 21.0 s for the guest coronene-d_{12}. Furthermore, a 4,4'-Br substituted DBI was used to form host-guest RTP systems with 15 different aromatic guest molecules, to tune the phosphorescence emission color from blue to red and to demonstrate the versatility of the host. Mechanistic insights were gained through a host-guest-matrix system which shows RTP already by trace combinations of a 4,4'-Br DBI host (0.10 wt%) and a pyrene-d_{10} guest (0.01 wt%) in an otherwise non-RTP-emissive aromatic matrix.

Introduction

The design of efficient phosphorescent emitters frequently involves the incorporation of heavy transition metals, such as d^8 or d^{10} metals.[1,2] The development of purely organic materials showing room temperature phosphorescence (RTP) is more challenging, but significant progress has been achieved in recent years including phosphorescence with ultra-long lifetimes in the range of seconds.[3–5] Due to their unique afterglow properties, RTP materials found applications in encryption, anti-counterfeiting and high-resolution bio-imaging, amongst others.[6,7] The development of new, efficient RTP materials still remains challenging and repeatedly consists of trial-and-error approaches.[8,9]

Key challenges in realizing organic RTP are the efficient population and stabilization of triplet excited states for high quantum yields and long phosphorescence lifetimes.[10–12] Synthetic strategies to achieve RTP compounds and materials are the use of polymers,[13–16] supramolecular assemblies,[17] molecular aggregates,[18–20] carbon dots[21–23] or through crystallization.[24,25]

Host-guest RTP systems are promising candidates for realizing organic RTP, generally consisting of a solid compound that acts as a matrix (host) and a phosphorescent dopant (guest) in high dilution.[26–29] The variety of studied hosts and/or guests in these literature examples is generally small and the general design of most of these systems leave little room for straightforward variations.[30–39]

In an increasing number of cases, the RTP emission of a compound was found to arise from incorporated trace impurities, making them in reality host-guest RTP systems.[40–44] Identifying these impurities, or even just proving their existence, can be very challenging as RTP may arise even already at ppb levels of contamination.[45] Therefore, host-guest systems steadily gain in importance among purely-organic RTP materials. Among purely organic RTP materials, isophthalic acid is a compound with outstanding RTP properties as a crystalline solid.[46,47] It is also capable of serving as a host compound for host-guest RTP.[48] Polymeric isophthalic acid esters have also been shown to be capable of RTP.[49]

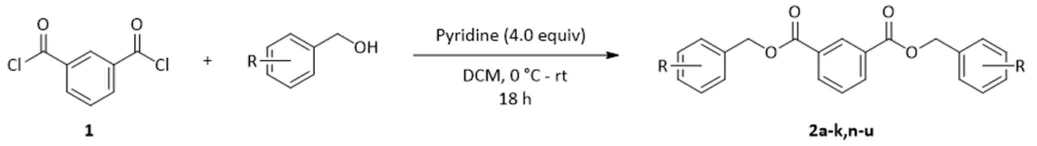
In this study, we show that a series of simple, substituted dibenzyl isophthalates (DBIs) serve as versatile hosts to enable color-tunable RTP across the spectrum from blue to red. A mechanistic analysis further provides insights into the RTP process, supporting the potential of DBIs for future development as minimalistic RTP host-guest materials.

Results and Discussion

Initial discovery

Intrigued by the known photophysical properties of isophthalic acid and its derivatives, we investigated isophthalic acid esters as possible hosts for RTP host-guest systems.

We synthesized a diverse set of 21 DBIs (**2a**-**2u**) in yields of 50% to 91% to gauge the effect of functional groups at the benzylic ester moiety on the RTP properties of the studied host-guest systems. DBIs could be synthesized using isophthaloyl dichloride (**1**) in a simple, pyridine-catalyzed one step substitution reaction (Scheme 1) and free of RTP-causing trace impurities (see ESI chapter 5.2 for details).



2a R = H (91 %) **2b** R = 4-Cl (89 %) **2c** R = 2-Br (69 %) **2d** R = 3-Br (83 %) **2e** R = 4-Br (83 %) **2f** R = 4-Br-2-OMe (69 %) **2g** R = 4-I (93 %) **2h** R = 4-OMe (86 %) **2i** R = 4-(OPh(4-OMe)) (65 %) **2j** R = 4-(OPh(4-Br)) (62 %) **2k** R = 4-SMe (91 %) **2n** R = 4-SPh (50 %) **2o** R = 4-(SPh(4-SMe)) (71 %) **2p** R = 4-(SPh(4-Br)) (72 %) **2q** R = 4-CHO (54 %) **2r** R = 4-CN (74 %) **2s** R = 4-CO_2Me (44 %) **2t** R = 4-CF_3 (75 %) **2u** R = 4-$B(OH)_2$ (26 %)

Scheme 1 Scope of the dibenzyl isophthalates synthesized in this work via nucleophilic substitution of isophthaloyl dichloride (1) with substituted benzyl alcohols. The esters 2l (R = 4-S(O)Me) and 2m (R = 4-SO_2Me) were synthesized by oxidation of 2k. For detailed data, see ESI chapter 5.2.

DBI host-guest systems with coronene

As a benchmark, we doped 0.1 wt% of coronene guest (**3**) into the observed hosts (Table 1).[37] Melt-cast samples of host-guest systems were formed by addition of a solution of the guest to the host, followed by solvent evaporation and melting of the mixture under vacuum. After cooling to rt, solid host-guest systems were obtained (see ESI chapter 1.4 for details).

To our delight, all coronene (**3**) doped DBIs showed RTP. To the best of our knowledge, this presents the first study of a host being functionalized with a multitude of functional groups (>20) and still showing RTP in almost all cases.

Phosphorescence spectra of these composites with 0.1 wt% coronene (**3**) showed emission from 500-700 nm, with the main emission features being slightly hypsochromically shifted for bromine and iodine substituted DBIs. (see Figure 1 for representative examples). As expected, the presence of a bromine or iodine substituent significantly increased RTP quantum yields due to the heavy-atom effect.[50,51] This trend can be rationalized by comparing RTP quantum yields of the unsubstituted parent dibenzyl isophthalate **2a**, (φ_{Phos} = 0.4 %) to the *para*-substituted halide analogues 4-Cl (**2b**, 6.2 %) < 4-Br (**2e**, 10.5 %) < 4-I (**2g**, 42.5 %). Phosphorescent lifetimes decreased from **2b** to **2g** (Table 1).

The influence of the substitution position on the phosphorescence was probed by synthesizing the *ortho*- and *meta*-analogs of the 4-Br substituted DBI (**2e**). The 2-Br DBI (**2c**, φ_{Phos} = 13.6 %) showed at comparable RTP quantum yield to **2e**, while that of 3-Br DBI (**2d**, φ_{Phos} = 3.0 %) was significantly lower. Interestingly, inserting a methoxy group as in 4-Br-2-OMe DBI (**2f**, φ_{Phos} = 26.5 %), the quantum yield increased significantly compared to **2e**. These findings illustrate that a small variation in the substitution pattern of the benzyl esters can lead to strong changes in ϕ_{Phos} and highlight the potential of DBIs as tunable hosts for organic RTP materials. This effect was also apparent in modifications of 4-SMe DBI (**2k**). Incorporation of a

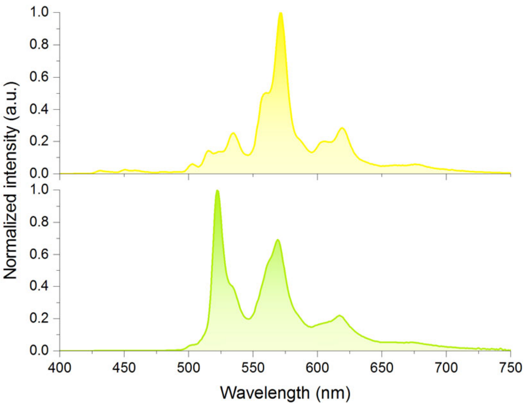


Figure 1 Phosphorescence spectra of the (top) coronene@4-CN DBI and (bottom) coronene@4-Br-2-OMe DBI host-guest systems. Excitation at 350 nm.

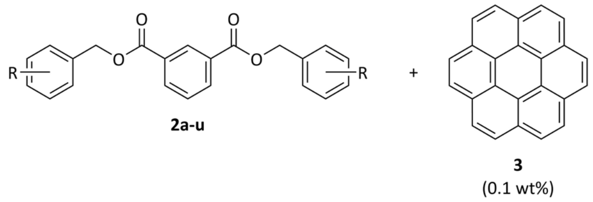


Table 1 Phosphorescence lifetimes and quantum yields of DBIs with 0.1 wt% coronene (**3**); melt-cast samples under ambient conditions.[a] The three highest phosphorescence lifetimes and quantum yields have been highlighted. For more details, see ESI chapter 3.2.

No.	R =	τ_P [b c d]	φ_{total} [d] [%]	φ_{Fl} [%]	φ_{Phos} [%]
2a	all H	5.11 s	13.2	12.8	0.4
2b	4-Cl	6.20 s	17.8	11.6	6.2
2c	2-Br	1.58 s	19.4	5.8	13.6
2d	3-Br	1.77 s	10.2	7.2	3.0
2e	4-Br	3.61 s	16.5	6.0	10.5
2f	4-Br-2-OMe	1.29 s	31.0	4.5	**26.5**
2g	4-I	65 ms	42.5	<0.1	**42.5**
2h	4-OMe	5.70 s	24.6	22.2	2.4
2i	4-(OPh(4-OMe))	3.08 s	11.0	9.9	1.1
2j	4-(OPh(4-Br))	0.94 s	18.9	9.2	9.7
2k	4-SMe	5.13 s	13.0	8.8	4.2
2l	4-S(O)Me	5.36 s	33.8	31.9	1.9
2m	4-SO_2Me	4.91 s	8.4	6.9	1.5
2n	4-SPh	**6.46 s**	23.3	19.6	3.7
2o	4-(SPh(4-SMe))	2.12 s	21.7	20.7	1.0
2p	4-(SPh(4-Br))	1.95 s	23.6	3.8	**19.8**
2q	4-CHO	4.57 s	3.6	2.6	1.0
2r	4-CN	**6.39 s**	16.0	13.2	2.8
2s	4-CO_2Me	5.17 s	23.8	19.0	4.8
2t	4-CF_3	3.27 s	42.3	42.3	<0.1
2u	4-$B(OH)_2$	**6.32 s**	12.5	11.5	1.0

[a] Excitation at 350 nm. [b] Average lifetimes from multi-exponential decays (mono-exponential exceptions: Entries 2, 14, 18). [c] Emission measurement at 570 nm for RTP lifetime determination. [d] See ESI for details on the determination of the quantum yields and lifetimes.

thioether slightly raised φ_{Phos} of **2k** (φ_{Phos} = 4.2 %) in comparison to the oxygen analogue 4-OMe DBI (**2h**, φ_{Phos} = 2.4 %). An extension of the π-system to 4-(OPh(4-OMe)) DBI (**2i**) and 4-(SPh(4-SMe)) DBI (**2o**) lowered both RTP quantum yields and lifetimes. On the other hand, substitution of the methyl ether or thioether with a *p*-bromophenol- or *p*-thiophenol-(thio)ether strongly increased RTP quantum yields up to φ_{Phos} = 19.8 % (**2p**).

When the methyl thioether was changed to a phenyl thioether (4-SPh DBI, **2n**) φ_{Phos} decreased slightly to 3.7 % compared to **2k**. However, the RTP lifetime increased to the highest of all investigated DBIs with τ = 6.46 s. To the best of our knowledge, this is the longest measured RTP lifetime of coronene (**3**) in a purely organic host-guest RTP system, longer than **3** in a poly(methyl methacrylate) (PMMA) matrix[52] or in β-estradiol.[53] Both have reported RTP lifetimes of τ_{Phos} = 6.0 s.

DBI host-guest systems with coronene-d_{12}

The observed long lifetime of coronene@4-SPh DBI (**2n**), prompted us to investigated the influence of deuterated coronene (**3**) on the RTP lifetimes and quantum yields for selected hosts (Figure 2), as deuteration of guests can drastically improve RTP lifetimes and quantum yields[39,54,55] and host-guest systems with coronene-d_{12} have been reported to exhibit RTP lifetimes of close to or over 20 s.[52,56,57] For comparison, we chose four DBIs with the longest lifetimes from Table 1, as well as 4-Br DBI (**2e**) for its balanced RTP lifetime and quantum yield. 4-I DBI (**2g**) was selected due to its high RTP quantum yield.

Coronene-d_{12} doped (0.1 wt%) 4-Br DBI (**2e**) and 4-I DBI (**2g**), showed an increase in RTP lifetime compared to the non-deuterated host-guest systems of up to 60 %. For the other DBIs, RTP lifetime was increased approximately 2.5 fold in each case. (Figure 2a). The coronene-d_{12}@4-CN DBI (**2r**) host-guest system showed the longest RTP lifetime of τ = 21.0 s (Figures 2c,d). This lifetime is longer than the previous record lifetime of a purely-organic, non-polymeric host-guest RTP system with β-estradiol as the host compound (τ = 17.0 s).[56] Moreover, the lifetime of the coronene-d_{12}@4-CN DBI (**2r**) system was only slightly shorter than that of coronene-d_{12} in PMMA (τ = 23 s)[52] and of coronene-d_{12} in the metal-organic framework ZIF-8 (τ = 22.4 s),[57] which are the host-guest systems with the currently longest known RTP lifetimes of coronene-d_{12}.

RTP quantum yields also increased through deuteration of **3**. 4-B(OH)$_2$ DBI (**2u**) showed the smallest absolute increase in φ_{Phos}, from 1.0 % to 2.0 %. 4-CN DBI (**2r**), 4-Cl DBI (**2b**), 4-Br DBI (**2e**) and 4-SPh DBI (**2n**) all showed an increase in RTP quantum yield by a factor of 2.5. For 4-OMe DBI (**2h**) we observed an increase with a factor of 3.6 (Figure 2b). 4-I DBI (**2g**) showed the smallest relative increase in RTP quantum yield, but showed an extremely high φ_{Phos} of 76.7 %.

Host-guest RTP from 4-Br DBI with different guests

Motivated by our findings, we targeted color tunable host-guest systems. **2e** was employed as a host, due to the balanced RTP quantum yield and lifetime values of coronene (**3**)@4-Br DBI (**2e**). To achieve emission colors of the full visible spectrum, we focused on the readily available aromatic compounds **G1** - **G15** (Figure 3).

Upon synthesizing 4-SMe DBI (**2k**), we could identify 4-(methylthio)-benzaldehyde (**G1**) as an RTP causing trace impurity (**G1**). Now using **G1** as guest in 4-Br DBI (**2e**), it also caused blue-green RTP. Substituting the thiomethyl residue for a 4-bromophenylthioether caused a 3.5-fold increase in RTP QY from 2.8 % for **G1** to 9.8 % for **G2**. Similar to **G1**, RTP was also obtained by doping 4-(dimethylamino)benzaldehyde (**G3**) into **2e**. The RTP of **G3** in a host-guest system has been described before,[33] but no maximum at 613 nm was reported in the RTP emission spectrum. This maximum might be attributed to the long wave emission band (LE), arising from a twisted intramolecular charge-transfer state (TICT) of **G3**.[58,59]

Many polycyclic aromatic hydrocarbons showed RTP with **2e**, highlighting the versatility of this simple, non-polymeric host compound. Compounds such as naphthalene derivatives **G4** - **G6** and the structurally related fluoranthene (**G7**),[60–65] benzophenanthrene isomers **G8** - **G11**,[66–69] and benzo-[*ghi*]perylene (**G15**)[70–72] allowed us to prepare host-guest RTP systems with colors ranging from yellow to deep red. Some of these guests have been described before in host-guest RTP

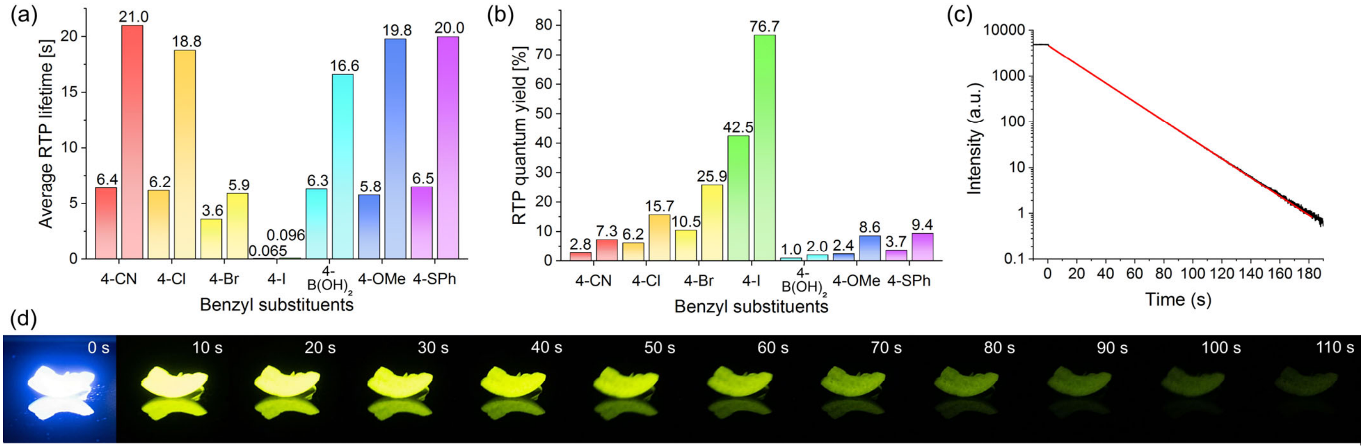


Figure 2 (a) Comparison of the lifetimes of DBI host-guest systems with coronene (**3**) as a guest (0.1 wt%, left columns) and with coronene-d_{12} as a guest (0.1 wt%, right columns). (b) Comparison of the RTP quantum yields of DBI host-guest systems with coronene (**3**) as a guest (0.1 wt%, left columns) and with coronene-d_{12} as a guest (0.1 wt%, right columns). (c) Lifetime decay curve (black line) and exponential tail fit (red line) of the coronene-d_{12}@4-CN DBI host-guest system (emission at 570 nm). Excitation at 350 nm for a), b) ,c). (d) Photographs of the luminescence of the coronene-d_{12}@4-CN DBI host-guest system under irradiation with a 365 nm flashlight and after its removal. For detailed data, see ESI chapter 3.3.

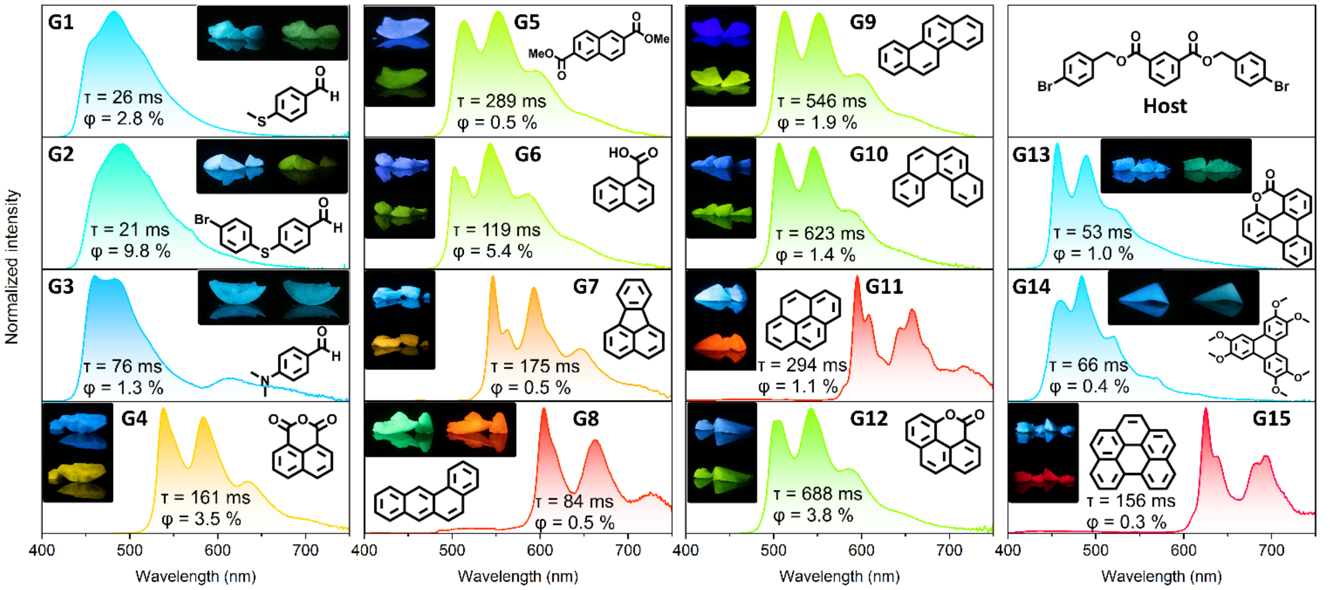


Figure 3 RTP emission spectra of guests (0.1 wt%) in 4-Br DBI (**2e**). The RTP quantum yield and average lifetimes are annotated. The photographs show the steady-state luminescence (left or top pictures) and the phosphorescence after removal of the light source (right or bottom pictures). Samples were excited with a 365 nm flashlight for photographs. For detailed measurement data (excitation wavelengths, quantum yields and lifetimes) see ESI chapter 4.1.

systems (see ESI Table S5 for a comparison). For **G10**, to our best knowledge, there has not been a report of RTP yet except for a (currently) non-peer-reviewed study.[73]

Pyrene (**G11**) and its fully deuterated counterpart are well-studied compounds for host-guest RTP systems, but it is difficult to achieve notable quantum yields.[56,61,74–77] For comparison, we also investigated host-guest systems with pyrene-d_{10} in **2e**, **2b** and **2g** (see ESI chapter 4.3 and ESI Table S6 for details), yielding RTP QY of up to 4.1 %.

The only benzophenanthrene isomer that did not show RTP with **2e** was triphenylene, which was expected to show blue RTP.[78] Instead, we could obtain blue RTP by employing the literature-known guest **G14**.[79] Moreover, neither unsubstituted naphthalene nor phenanthrene showed RTP as guests.

Since the introduction of acids, esters and anhydrides seemed to enable RTP for naphthalene derivatives **G4** - **G6** with **2e**, we applied this structural principle to phenanthrene and triphenylene, and synthesized **G12** and **G13** (see ESI chapter 5.3 for details). A similar functionalization was recently used by Yu and coworkers to boost the RTP properties of coronene (**3**) as a guest by substituting it with esters.[80] Incorporating **G12** and **G13** into **2e** showed green and blue RTP respectively, with RTP spectrums close to their unsubstituted counterparts.[78] Unfortunately, **G13** proved to be light-sensitive in the host-guest system and degraded quickly upon irradiation, which might have contributed to the low RTP quantum yield.

Material properties of DBIs

Our host-guest systems are not limited to a crystalline environment. When cotton wool is soaked with a DCM solution of small amounts of 4-Br DBI (**2e**) and fluoranthene (**G7**), the resulting wool displayed RTP after drying under air (Figure 4a). Despite the low RTP quantum yield of the **G7**@4-Br DBI host-guest system, the afterglow was easily visible by eye in a dark room.

Phosphorescence is also induced if the DBI host is present only in trace amounts and when both, DBI and guest, are embedded in a crystalline matrix together. When we prepared a melt-cast sample from *p*-toluic acid (99.99 wt%) and pyrene-d_{10}, (0.01 wt%), no RTP was observed after UV-irradiation. However, when 4-Br DBI (**2e**) was added in trace amounts (0.1 wt%), red RTP could be observed (Figure 4b, see also ESI chapter 4.3 for details).

Finally, we found that selected DBIs showed gelation-type behavior when solutions in organic solvents were diluted with protic solvents. As a representative example, we diluted a dichloromethane (DCM) solution of **G12**@4-SMe DBI (**2k**) with methanol and found near instant gelation-like solidification of the solution (Figure 4c). The solidified mixture was self-standing upon inversion of the vial, indicative of an organogel. It further showed the green RTP of **G12**. This result suggests that DBIs could be utilized as phosphorescent low-molecular weight gelators in the future. A similar result was recently reported by Xiang and co-workers, who prepared carbazole-derived amides of different (aromatic) acids as organogelators, including one of isophthalic acid.[81]

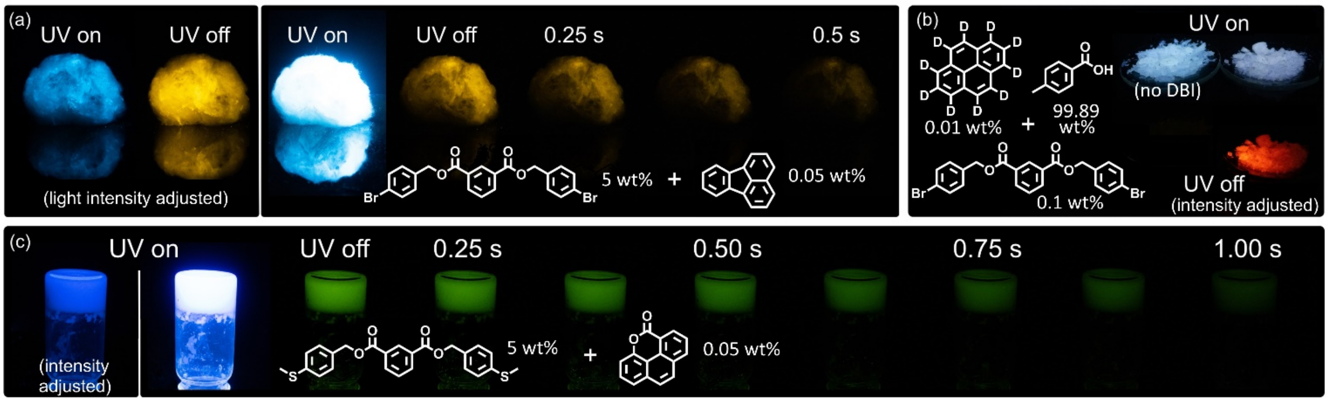


Figure 4 (a) Cotton wool after soaking it with a DCM solution of 4-Br DBI (**2e**) (5 wt%) and fluoranthene (**G7**) (0.05 wt%) and drying in air. (b) Two melt-cast samples from *p*-toluic acid (99.89 wt%), 4-Br DBI (**2e**) (0.1 wt%) and pyrene-d_{10} (0.01 wt%). The left sample was prepared without the DBI as a control. (c) Self-standing gel or gel-like precipitate from 4-SMe DBI (**2k**) (5 wt%) and **G12** (0.05 wt%) from a DCM solution by addition of MeOH (wt% refers to the total wt% after MeOH addition; 1:1 mixture of MeOH and DCM). Photographs of samples under UV irradiation (365 nm flashlight) and after removing the light source.

TD-DFT Computations and mechanistic considerations

From Figure 4b, it is apparent that the RTP of the pyrene-d_{10}@4-Br DBI (**2e**) system arises more likely from the interaction of a single pair of molecules, rather than aggregation in form of clusters or a certain crystal phase. For this reason, we investigated a single pair of host and guest for time-dependent density functional theory (TD-DFT) computations.

TD-DFT computations were conducted with 4-Br DBI (**2e**) as the host and coronene (**3**), pyrene (**G11**) and the lactones **G12** and **G13** as guests. In the optimized gas-phase geometries, the benzyl residues of **2e** are tilted towards the planar guest molecules.

A requirement for efficient intersystem crossing is the presence of excited singlet and triplet states being energetically within < 0.1 eV, which was found in all four investigated systems (Table S7). The excitation from the ground state guest@4-Br DBI (**2e**) to excited singlet states involves both the host and the guest (see ESI Figures S171-174). Inspection of the natural transition orbitals participating in the transitions revealed that the excitation is either of almost pure charge-transfer character as e.g. for coronene (**3**) (Figure 5, left), or involves both the host and guest as for the lactones **G12** and **G13** (Figure 5, right). This result is in agreement with findings by Yang et al., who showed the importance charge-transfer between host and guest to realize RTP.[82]

The computed differences of the adiabatic energies (E_{adia} and E_{0-0}) of the S_0 and T_1 are in reasonable agreement with the experimentally obtained phosphorescent energies (see ESI Table S8), reproducing the observed color tunability of the systems. The spin density of the T_1 state resides in all cases on the guest, suggesting that the observed phosphorescence stems from the guest (Figure 6 and ESI Figure S175).

Pyrene (**G11**) is known to form exciplexes which can rapidly accelerate the ISC process.[83,84] When we tested the influence of different doping amounts of pyrene-d_{10} on the fluorescence and RTP emission spectra of the pyrene-d_{10}@4-Br DBI (**2e**) host-guest system, the excimer fluorescence of pyrene-d_{10} at 469 nm decreased with decreasing guest amounts (see ESI chapter 4.2 for details). This indicates an origin of excimer emission solely from the pyrene dimer interactions in the solid state, rather than an exciplex between pyrene-d_{10} and **2e**.[85] For isophthalic acid, its RTP is thought to be enabled by hyperfine coupling in a radical ion pair (RIP), as RIPs were shown to be involved in the mechanism of the RTP.[46] Similarly, the RTP of benzoindole derivatives was recently shown to involve radical cations.[32]

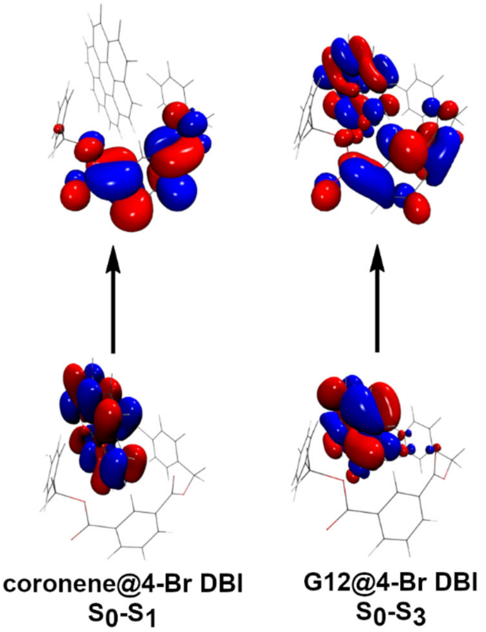


Figure 5 Natural transition orbitals (NTO) for TD-DFT computed $S_0 \rightarrow S_n$ transitions of coronene@4-br DBI (left) and G12@4-Br DBI (right).

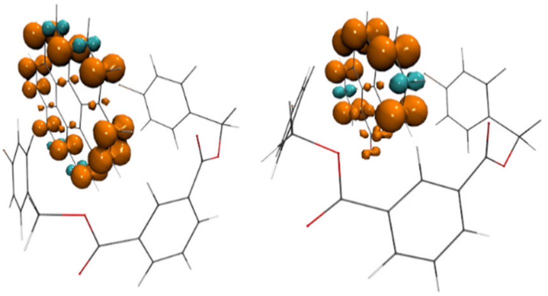


Figure 6 Spin density of T_1-state of coronene@4Br DBI (left) and **G12**@4-Br DBI (right) representation at +0.005/–0.005 e bohr^{-3} (orange/cyan).

Hence, we assume that the respective guest and DBI form an excited singlet state, which turns into a RIP. The singlet RIP then undergoes rapid ISC to a triplet RIP, which recombines to yield the guest in the triplet state and the DBI in the ground state.[86] The radiative emission of the triplet guest is then observed as RTP. A similar mechanism was also suggested by Ma et al. very recently for the **G10**@benzophenone host-guest RTP system and for other PAH guests with the same host.[73]

Conclusions

In conclusion, we have shown that dibenzyl isophthalates (DBIs) are versatile and easily accessible hosts for room temperature phosphorescence (RTP). Host-guest RTP systems with coronene (**3**) and coronene-d_{12} as guests showed RTP properties that rival or exceed comparable state-of-the-art host-guest RTP systems. Namely, the coronene-d_{12}@4-I DBI (**2g**) system could achieve a RTP quantum yield of 76.7 % while 4-CN DBI (**2r**) as a host let to a RTP lifetime of 21.0 s with the same guest. Furthermore, the versatility of 4-Br DBI (**2e**) as a host was shown by employing 15 different guests to construct host-guest RTP systems, emitting colors ranging from blue to red. The properties of DBIs which could lead to the development of RTP material applications of DBIs were outlined A mechanism for the RTP of DBIs and guests was formulated which could help to further understand the phenomenon of host-guest RTP. In the future, we expect the development of more structurally diverse isophthalates as hosts for RTP applications.

Data availability

For full experimental procedures, and spectroscopic and analytical data for all new compounds including copies of NMR spectra, see the ESI. Notably, a full, concise summary of all photophysical data is presented in ESI chapter 2.

Author Contributions

M.M. and B.J.N. conceived the project. M.M. performed the syntheses, photophysical experiments and routine analytics. E.H. performed the DFT calculations. All authors designed the experiments and participated in writing and reviewing of the manuscript.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

We thank M.Sc. Jonas Bentrup and M.Sc. Luisa Plitzko (both University of Bremen) for their help with some of the initial synthetic work.

Notes and references

1 V. W.-W. Yam, V. K.-M. Au and S. Y.-L. Leung, Light-Emitting Self-Assembled Materials Based on d(8) and d(10) Transition Metal Complexes, *Chem. Rev.*, 2015, **115**, 7589.

2 M.-C. Tang, M.-Y. Chan and V. W.-W. Yam, Molecular Design of Luminescent Gold(III) Emitters as Thermally Evaporable and Solution-Processable Organic Light-Emitting Device (OLED) Materials, *Chem. Rev.*, 2021, **121**, 7249.

3 H. Ma, A. Lv, L. Fu, S. Wang, Z. An, H. Shi and W. Huang, Room-Temperature Phosphorescence in Metal-Free Organic Materials, *Ann. Phys.*, 2019, **531**, 1800482.

4 Y. Liu, G. Zhan, Z.-W. Liu, Z.-Q. Bian and C.-H. Huang, Room-temperature phosphorescence from purely organic materials, *Chin. Chem. Lett.*, 2016, **27**, 1231.

5 Z. Wu, J. Nitsch and T. B. Marder, Persistent Room-Temperature Phosphorescence from Purely Organic Molecules and Multi-Component Systems, *Adv. Opt. Mater.*, 2021, **9**, 2100411.

6 S. Xu, R. Chen, C. Zheng and W. Huang, Excited State Modulation for Organic Afterglow: Materials and Applications, *Adv. Mater.*, 2016, **28**, 9920.

7 H. Chen, X. Yao, X. Ma and H. Tian, Amorphous, Efficient, Room-Temperature Phosphorescent Metal-Free Polymers and Their Applications as Encryption Ink, *Adv. Opt. Mater.*, 2016, **4**, 1397.

8 S. Chanmungkalakul, C. Wang, R. Miao, W. Chi, D. Tan, Q. Qiao, E. C. X. Ang, C.-H. Tan, Y. Fang, Z. Xu and X. Liu, A Descriptor for Accurate Predictions of Host Molecules Enabling Ultralong Room-Temperature Phosphorescence in Guest Emitters, *Angew. Chem. Int. Ed.*, 2022.

9 L. Gu, X. Wang, M. Singh, H. Shi, H. Ma, Z. An and W. Huang, Organic Room-Temperature Phosphorescent Materials: From Static to Dynamic, *J. Phys. Chem. Lett.*, 2020, **11**, 6191.

10 A. D. Nidhankar, Goudappagouda, V. C. Wakchaure and S. S. Babu, Efficient metal-free organic room temperature phosphors, *Chem. Sci.*, 2021, **12**, 4216.

11 S. Hirata, Recent Advances in Materials with Room-Temperature Phosphorescence: Photophysics for Triplet Exciton Stabilization, *Adv. Opt. Mater.*, 2017, **5**, 1700116.

12 Kenry, C. Chen and B. Liu, Enhancing the performance of pure organic room-temperature phosphorescent luminophores, *Nat. Commun.*, 2019, **10**, 2111.

13 H. Gao and X. Ma, Recent progress on pure organic room temperature phosphorescent polymers, *Aggregate*, 2021, **2**.

14 F. Gu and X. Ma, Stimuli-Responsive Polymers with Room-Temperature Phosphorescence, *Chem. Eur. J.*, 2022, **28**, e202104131.

15 Y. Wang, W. Ye, T. Cao, C. Wang, H. Meng, Z. Gao and C. Wang, Metal-Free organic polymeric room temperature phosphorescence system with Multi-Colour and ultralong lifetime, *Chemical Engineering Journal*, 2024, **481**, 148642.

16 Y. Liang, P. Hu, H. Zhang, Q. Yang, H. Wei, R. Chen, J. Yu, C. Liu, Y. Wang, S. Luo, G. Shi, Z. Chi and B. Xu, Enabling Highly Robust Full-Color Ultralong Room-Temperature Phosphorescence and Stable White Organic Afterglow from

Polycyclic Aromatic Hydrocarbons, *Angew. Chem. Int. Ed.*, 2024, **63**, e202318516.
17 X.-K. Ma and Y. Liu, Supramolecular Purely Organic Room-Temperature Phosphorescence, *Acc. Chem. Res.*, 2021.
18 T. Wu, J. Huang and Y. Yan, From aggregation-induced emission to organic room temperature phosphorescence through suppression of molecular vibration, *Cell Rep. Phys. Sci.*, 2022, **3**, 100771.
19 W. Zhao, Z. He and B. Z. Tang, Room-temperature phosphorescence from organic aggregates, *Nat. Rev. Mater.*, 2020, **5**, 869.
20 Q. Peng, H. Ma and Z. Shuai, Theory of Long-Lived Room-Temperature Phosphorescence in Organic Aggregates, *Acc. Chem. Res.*, 2021, **54**, 940.
21 J. Li, Y. Wu and X. Gong, Evolution and fabrication of carbon dot-based room temperature phosphorescence materials, *Chem. Sci.*, 2023, **14**, 3705.
22 X. Wei, J. Yang, L. Hu, Y. Cao, J. Lai, F. Cao, J. Gu and X. Cao, Recent advances in room temperature phosphorescent carbon dots: preparation, mechanism, and applications, *J. Mater. Chem. C*, 2021, **9**, 4425.
23 Y. Sun, X. Zhang, J. Zhuang, H. Zhang, C. Hu, M. Zheng, B. Lei and Y. Liu, The room temperature afterglow mechanism in carbon dots: Current state and further guidance perspective, *Carbon*, 2020, **165**, 306.
24 W. Jia, Q. Wang, H. Shi, Z. An and W. Huang, Manipulating the Ultralong Organic Phosphorescence of Small Molecular Crystals, *Chem. Eur. J.*, 2020, **26**, 4437.
25 M. Baroncini, G. Bergamini and P. Ceroni, Rigidification or interaction-induced phosphorescence of organic molecules, *Chem. Commun.*, 2017, **53**, 2081.
26 X. Yan, H. Peng, Y. Xiang, J. Wang, L. Yu, Y. Tao, H. Li, W. Huang and R. Chen, Recent Advances on Host-Guest Material Systems toward Organic Room Temperature Phosphorescence, *Small*, 2021, e2104073.
27 S. Guo, W. Dai, X. Chen, Y. Lei, J. Shi, B. Tong, Z. Cai and Y. Dong, Recent Progress in Pure Organic Room Temperature Phosphorescence of Small Molecular Host–Guest Systems, *ACS Mater. Lett.*, 2021, **3**, 379.
28 J. Li, G. Wang, X. Chen, X. Li, M. Wu, S. Yuan, Y. Zou, X. Wang and K. Zhang, Manipulation of Triplet Excited States in Two-Component Systems for High-Performance Organic Afterglow Materials, *Chem. Eur. J.*, 2022, e202200852.
29 G. Qu, Y. Zhang and X. Ma, Recent progress on pure organic room temperature phosphorescence materials based on host-guest interactions, *Chin. Chem. Lett.*, 2019, **30**, 1809.
30 Y. Sun, J. Liu, J. Li, X. Li, X. Wang, G. Wang and K. Zhang, Manipulation of Triplet Excited States for Long-Lived and Efficient Organic Afterglow, *Adv. Opt. Mater.*, 2021, 2101909.
31 S. Ding, X. Wang, G. Wang, M. Wu, J. Li, X. Zhao, H. Li, S. Ren and K. Zhang, A Twisted Phosphor: Breaking T 1 Energy Conservation in Dopant-Matrix Organic Phosphorescence Systems, *Adv. Opt. Mater.*, 2022, 2202540.
32 C. Qian, Z. Ma, X. Fu, X. Zhang, Z. Li, H. Jin, M. Chen, H. Jiang, X. Jia and Z. Ma, More than Carbazole Derivatives Activate Room Temperature Ultralong Organic Phosphorescence of Benzoindole Derivatives, *Adv. Mater.*, 2022, **34**, e2200544.
33 B. Ding, L. Ma, Z. Huang, X. Ma and H. Tian, Engendering persistent organic room temperature phosphorescence by trace ingredient incorporation, *Sci. Adv.*, 2021, **7**.
34 S. Feng, Q. Huang, S. Yang, Z. Lin and Q. Ling, A metal-free 2D layered organic ammonium halide framework realizing full-color persistent room-temperature phosphorescence, *Chem. Sci.*, 2021, **12**, 14451.
35 Y. Lei, J. Yang, W. Dai, Y. Lan, J. Yang, X. Zheng, J. Shi, B. Tong, Z. Cai and Y. Dong, Efficient and organic host–guest room-temperature phosphorescence: tunable triplet–singlet crossing and theoretical calculations for molecular packing, *Chem. Sci.*, 2021, **12**, 6518.
36 M. Li, X. Cai, Z. Chen, K. Liu, W. Qiu, W. Xie, L. Wang and S.-J. Su, Boosting Purely Organic Room-Temperature Phosphorescence Performance through Host-Guest Strategy, *Chem. Sci.*, 2021.
37 M. Wu, X. Wang, Y. Pan, J. Li, X. Li, Y. Sun, Y. Zou, H. Zhang and K. Zhang, Two-Component Design Strategy: Achieving Intense Organic Afterglow and Diverse Functions in Coronene-Matrix Systems, *J. Phys. Chem. C*, 2021, **125**, 26986.
38 Y. Lei, W. Dai, Y. Tian, J. Yang, P. Li, J. Shi, B. Tong, Z. Cai and Y. Dong, Revealing Insight into Long-Lived Room-Temperature Phosphorescence of Host-Guest Systems, *J. Phys. Chem. Lett.*, 2019, **10**, 6019.
39 S. Hirata, K. Totani, J. Zhang, T. Yamashita, H. Kaji, S. R. Marder, T. Watanabe and C. Adachi, Efficient Persistent Room Temperature Phosphorescence in Organic Amorphous Materials under Ambient Conditions, *Adv. Funct. Mater.*, 2013, **23**, 3386.
40 Z. Wu, J. C. Roldao, F. Rauch, A. Friedrich, M. Ferger, F. Würthner, J. Gierschner and T. B. Marder, Pure Boric Acid Does Not Show Room Temperature Phosphorescence (RTP), *Angew. Chem. Int. Ed.*, 2022.
41 C. Chen, Z. Chi, K. C. Chong, A. S. Batsanov, Z. Yang, Z. Mao, Z. Yang and B. Liu, Carbazole isomers induce ultralong organic phosphorescence, *Nat. Mater.*, 2021, **20**, 175.
42 A. Cheng, Y. Jiang, H. Su, B. Zhang, J. Jiang, T. Wang, Y. Luo and G. Zhang, Origin of Red-Shifted Phosphorescence from Triphenylamines: Triplet Excimer or Impurity?, *Angew. Chem. Int. Ed.*, 2022.
43 W. Qiao, M. Yao, J. Xu, H. Peng, J. Xia, X. Xie and Z. Li, Naphthyl Substituted Impurities Induce Efficient Room Temperature Phosphorescence, *Angew. Chem. Int. Ed.*, 2023, **62**, e202315911.
44 Z. Wu, K. Bergmann and Z. M. Hudson, Dopants Induce Persistent Room Temperature Phosphorescence in Triarylamine Boronate Esters, *Angew. Chem. Int. Ed.*, 2024, **63**, e202319089.

45 B. Chen, W. Huang, X. Nie, F. Liao, H. Miao, X. Zhang and G. Zhang, An Organic Host-Guest System Producing Room-Temperature Phosphorescence at the Parts-Per-Billion Level, *Angew. Chem. Int. Ed.*, 2021, **60**, 16970.
46 S. Kuno, H. Akeno, H. Ohtani and H. Yuasa, Visible room-temperature phosphorescence of pure organic crystals via a radical-ion-pair mechanism, *Phys. Chem. Chem. Phys.*, 2015, **17**, 15989.
47 Y. Gong, L. Zhao, Q. Peng, Di Fan, W. Z. Yuan, Y. Zhang and B. Z. Tang, Crystallization-induced dual emission from metal- and heavy atom-free aromatic acids and esters, *Chem. Sci.*, 2015, **6**, 4438.
48 X. Wang, Z. Wang, H. Feng, C. Lin, H. Shi, Z. An, Z.-M. Su and F.-S. Liang, Activating room-temperature phosphorescence of 1,8-naphthalimide by doping into aromatic dicarboxylic acid, *Chem. Commun.*, 2022.
49 Y.-F. Zhang, Y.-C. Wang, X.-S. Yu, Y. Zhao, X.-K. Ren, J.-F. Zhao, J. Wang, X.-Q. Jiang, W.-Y. Chang, J.-F. Zheng, Z.-Q. Yu, S. Yang and E.-Q. Chen, Isophthalate-Based Room Temperature Phosphorescence: From Small Molecule to Side-Chain Jacketed Liquid Crystalline Polymer, *Macromolecules*, 2019, **52**, 2495.
50 M. R. Wright, R. P. Frosch and G. W. Robinson, Phosphorescence Lifetime of Benzene. An Intermolecular Heavy-Atom Effect, a Deuterium Effect, and a Temperature Effect, *J. Phys. Chem. Phys.*, 1960, **33**, 934.
51 W. Dai, X. Niu, X. Wu, Y. Ren, Y. Zhang, G. Li, H. Su, Y. Lei, J. Xiao, J. Shi, B. Tong, Z. Cai and Y. Dong, Halogen Bonding: A New Platform for Achieving Multi-Stimuli-Responsive Persistent Phosphorescence, *Angew. Chem. Int. Ed.*, 2022.
52 J. L. Kropp and W. R. Dawson, Radiationless deactivation of triplet coronene in plastics, *J. Phys. Chem.*, 1967, **71**, 4499.
53 S. Hirata and I. Bhattacharjee, Vibrational Radiationless Transition from Triplet States of Chromophores at Room Temperature, *J. Phys. Chem. A*, 2021, **125**, 885.
54 N. Hirota and C. A. Hutchison, Effect of Deuteration of Durene on the Lifetime of the Phosphorescent Triplet State of Naphthalene in a Durene Host Crystal, *J. Phys. Chem. Phys.*, 1967, **46**, 1561.
55 S. H. Lin and R. Bersohn, Effect of Partial Deuteration and Temperature on Triplet-State Lifetimes, *J. Phys. Chem. Phys.*, 1968, **48**, 2732.
56 S. Hirata and M. Vacha, Large Reverse Saturable Absorption at the Sunlight Power Level Using the Ultralong Lifetime of Triplet Excitons, *J. Phys. Chem. Lett.*, 2017, **8**, 3683.
57 H. Mieno, R. Kabe, N. Notsuka, M. D. Allendorf and C. Adachi, Long-Lived Room-Temperature Phosphorescence of Coronene in Zeolitic Imidazolate Framework ZIF-8, *Adv. Opt. Mater.*, 2016, **4**, 1015.
58 A. Kawski, B. Kukliński and P. Bojarski, Excited state dipole moments of 4-(dimethylamino)benzaldehyde, *Chem. Phys. Lett.*, 2007, **448**, 208.
59 Z. R. Grabowski, K. Rotkiewicz and W. Rettig, Structural changes accompanying intramolecular electron transfer: focus on twisted intramolecular charge-transfer states and structures, *Chem. Rev.*, 2003, **103**, 3899.
60 X. Zhang, L. Du, W. Zhao, Z. Zhao, Y. Xiong, X. He, P. F. Gao, P. Alam, C. Wang, Z. Li, J. Leng, J. Liu, C. Zhou, J. W. Y. Lam, D. L. Phillips, G. Zhang and B. Z. Tang, Ultralong UV/mechano-excited room temperature phosphorescence from purely organic cluster excitons, *Nat. Commun.*, 2019, **10**, 5161.
61 H. Deng, G. Li, H. Xie, Z. Yang, Z. Mao, J. Zhao, Z. Yang, Y. Zhang and Z. Chi, Dynamic Ultra-long Room Temperature Phosphorescence Enabled by Amorphous Molecular "Triplet Exciton Pump" for Encryption with Temporospatial Resolution, *Angew. Chem. Int. Ed.*, 2024, **63**, e202317631.
62 H. Wu, L. Gu, G. V. Baryshnikov, H. Wang, B. F. Minaev, H. Ågren and Y. Zhao, Molecular Phosphorescence in Polymer Matrix with Reversible Sensitivity, *ACS Appl. Mater. Interfaces*, 2020, **12**, 20765.
63 R. Gahlaut, H. C. Joshi, N. K. Joshi, N. Pandey, P. Arora, R. Rautela, K. Suyal and S. Pant, Luminescence characteristics and room temperature phosphorescence of naphthoic acids in polymers, *J. Lumin.*, 2013, **138**, 122.
64 A. Salinas-Castillo, I. Sánchez-Barragán, J. M. Costa-Fernández, R. Pereiro, A. Ballesteros, J. M. González, A. Segura-Carretero, A. Fernández-Gutiérrez and A. Sanz-Medel, Iodinated molecularly imprinted polymer for room temperature phosphorescence optosensing of fluoranthene, *Chem. Commun.*, 2005, 3224.
65 I. Sánchez-Barragán, J. M. Costa-Fernández, R. Pereiro, A. Sanz-Medel, A. Salinas, A. Segura, A. Fernández-Gutiérrez, A. Ballesteros and J. M. González, Molecularly imprinted polymers based on iodinated monomers for selective room-temperature phosphorescence optosensing of fluoranthene in water, *Anal. Chem.*, 2005, **77**, 7005.
66 R. D. Burkhart, Kinetics of the delayed luminescence decay of 1,2-benzanthracene in polystyrene films, *Chem. Phys.*, 1980, **46**, 11.
67 M. M. Moodie and C. Reid, Inter- and Intramolecular Energy Transfer Processes. 3. Phosphorescence Bands of Some Carcinogenic Aromatic Hydrocarbons, *J. Phys. Chem. Phys.*, 1954, **22**, 252.
68 S. Hirata, Intrinsic Analysis of Radiative and Room-Temperature Nonradiative Processes Based on Triplet State Intramolecular Vibrations of Heavy Atom-Free Conjugated Molecules toward Efficient Persistent Room-Temperature Phosphorescence, *J. Phys. Chem. Lett.*, 2018, **9**, 4251.
69 L. Váňa, M. Jakubec, J. Sýkora, I. Císařová, J. Žádný, J. Storch and V. Církva, Synthesis of Azanhelicenes (n = 4-7) via Photocyclodehydrochlorination of 1-Chloro-N-aryl-2-naphthamides, *J. Org. Chem.*, 2022, **87**, 7150.
70 A. Salinas-Castillo, J. F. Fernández-Sánchez, A. Segura-Carretero and A. Fernández-Gutiérrez, Solid-surface phosphorescence characterization of polycyclic aromatic hydrocarbons and selective determination of

benzo(a)pyrene in water samples, *Analytica Chimica Acta*, 2005, **550**, 53.

71 A. Salinas Castillo, A. Segura Carretero, J. Costa Fernández, W. J. Jin and A. Fernández Gutiérrez, Heavy atom induced room temperature phosphorescence: a tool for the analytical characterization of polycyclic aromatic hydrocarbons, *Analytica Chimica Acta*, 2004, **516**, 213.

72 A. M. Alak and Vo Dinh Tuan, Selective enhancement of room temperature phosphorescence using cyclodextrin-treated cellulose substrate, *Anal. Chem.*, 1988, **60**, 596.

73 L. Ma, Y. Liu, T. Jiang, L. Zhou, Q. Wang, H. Tian and X. Ma, Ion-Radical Mediated Multi-Color Ultra-Long Afterglow Materials, *ChemRxiv [preprint]*, 2024, 10.26434/chemrxiv-2024-35nc4.

74 Y. A. Skryshevski and A. Y. Vakhnin, Excitation of phosphorescence of pyrene implanted into a photoconductive polymer, *Phys. Solid State*, 2007, **49**, 887.

75 J. J. Flynn, Z. M. Marsh, D. M. Krein, S. M. Wolf, J. E. Haley, E. S. Vasquez, T. M. Cooper, N. P. Godman and T. A. Grusenmeyer, Identification of Lithocholic Acid as a Molecular Glass Host for Room-Temperature Phosphorescent Materials, *ChemPhotoChem*, 2022, **6**.

76 Y. Xia, C. Zhu, F. Cao, Y. Shen, M. Ouyang and Y. Zhang, Host-Guest Doping in Flexible Organic Crystals for Room-Temperature Phosphorescence, *Angew. Chem. Int. Ed.*, 2022.

77 W. Qiu, X. Cai, M. Li, Z. Chen, L. Wang, W. Xie, K. Liu, M. Liu and S.-J. Su, Achieving Purely Organic Room-Temperature Phosphorescence Mediated by a Host-Guest Charge Transfer State, *J. Phys. Chem. Lett.*, 2021, **12**, 4600.

78 S. Hirata and M. Vacha, White Afterglow Room-Temperature Emission from an Isolated Single Aromatic Unit under Ambient Condition, *Adv. Opt. Mater.*, 2017, **5**, 1600996.

79 H. Wu, D. Wang, Z. Zhao, D. Wang, Y. Xiong and B. Z. Tang, Tailoring Noncovalent Interactions to Activate Persistent Room-Temperature Phosphorescence from Doped Polyacrylonitrile Films, *Adv. Funct. Mater.*, 2021, **31**, 2101656.

80 J. Yu, Z. Sun, H. Ma, C. Wang, W. Huang, Z. He, W. Wu, H. Hu, W. Zhao and W.-H. Zhu, Efficient Visible-Light-Activated Ultra-Long Room-Temperature Phosphorescence Triggered by Multi-Esterification, *Angew. Chem. Int. Ed.*, 2023, **62**, e202316647.

81 J. Xiang, Y. Shi, J. Jiang, J. Yan, S. Xiao, H. Lin and T. Yi, Color-Tunable Room Temperature Afterglow of Non-Conventional Organogels for Dynamic Anti-Counterfeiting, *Adv. Opt. Mater.*, 2023.

82 G. Yang, J. Li, X. Deng, X. Song, M. Lu, Y. Zhu, Z. Yu, B. Xu, M.-D. Li and L. Dang, Construction and Application of Large Stokes-Shift Organic Room Temperature Phosphorescence Materials by Intermolecular Charge Transfer, *J. Phys. Chem. Lett.*, 2023, **14**, 6927.

83 S. Hashimoto, Mechanism of fluorescence quenching of pyrene with purines in polar media: formation of the pyrene triplet state via exciplex formation, *J. Phys. Chem.*, 1993, **97**, 3662.

84 T. Okada, I. Karaki, E. Matsuzawa, N. Mataga, Y. Sakata and S. Misumi, Ultrafast intersystem crossing in some intramolecular heteroexcimers, *J. Phys. Chem.*, 1981, **85**, 3957.

85 A. Weller, Exciplex and radical pairs in photochemical electron transfer, *Pure Appl. Chem.*, 1982, **54**, 1885.

86 G. J. Kavarnos and N. J. Turro, Photosensitization by reversible electron transfer: theories, experimental evidence, and examples, *Chem. Rev.*, 1986, **86**, 401.