Controlling the fluorescence and room-temperature phosphorescence behaviour of carbon nanodots with inorganic crystalline nanocomposites

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There is a significant drive to identify alternative materials that exhibit room temperature phosphorescence for technologies including bio-imaging, photodynamic therapy and organic light-emitting diodes. Ideally, these materials should be non-toxic and cheap, and it will be possible to control their photoluminescent properties. This was achieved here by embedding carbon nanodots within crystalline particles of alkaline earth carbonates, sulphates and oxalates. The resultant nanocomposites are luminescent and exhibit a bright, sub-second lifetime afterglow. Importantly, the excited state lifetimes, and steady-state and afterglow colours can all be systematically controlled by varying the cations and anions in the host inorganic phase, due to the influence of the cation size and material density on emissive and non-emissive electronic transitions. This simple strategy provides a flexible route for generating materials with specific, phosphorescent properties and is an exciting alternative to approaches relying on the synthesis of custom-made luminescent organic molecules.
oom temperature phosphorescence (RTP) is traditionally associated with inorganic phases such as ZnS:Cu and SrAl2O4:Eu, Dy, where these exhibit afterglow lifetimes of minutes to hours. However, although ideal for applications such as emergency signage, they are less-suited to areas such as anti-counterfeiting and bio-imaging materials, where bright, sub-second afterglow is required. These compounds are also unstable in water and require large domain sizes (> 1 μm) for good performance. Significant efforts have therefore been made to develop alternative materials. For decades, RTP was only observed from organic materials at very low temperatures. As a major advance, it has now been shown that RTP can be observed in some transition metal complexes and N-heterocyclic molecular crystals, where intermolecular effects and enhanced structural rigidity facilitates RTP. Structural rigidity has also been achieved by embedding metal-free polyaromatic hydrocarbon (PAH) luminophores in porous media such as metal-organic frameworks, clays and cyclodextrins; or in amorphous matrices. Molecular crystals and PAHs show promise in sub-second afterglow applications, but the need for specific molecular design to give desired photoluminescent (PL) properties, known or predicted toxicity, and challenges associated with poor processability remain.

Carbon dots (CDs) provide an exciting alternative to these materials, and overcome many of the drawbacks, being water-soluble, cheap and easy to synthesise, and exhibiting excellent PL properties. Additionally, RTP is activated when they are integrated within host matrices such as poly(vinyl alcohol)13–15, amorphous silica16,17, and polyurethane. In this case, RTP originates from surface aromatic carbonyls and/or N-heterocycles, to which the host material prevents RTP quenching by molecular oxygen and hydrogen bonding confers rigidity. A few studies have also explored KAl(SO4)2·x(H2O)19, layered double hydroxides,21 and zeolites22 as inorganic host materials, where these demonstrated comparable RTP activation to polymer hosts. Calcite (CaCO3) has also been used as a host phase for CDs, yielding fluorescent nanocomposites, but no RTP was reported.

That CDs must be incorporated into a solid host to activate RTP suggests an exciting prospect—that it may be possible to tune the PL properties according to selection of the host material. Although polymeric hosts offer limited scope for varying atomic composition, inorganic materials can be synthesised using the periodic table of metal cations. Heavy atoms are predicted to influence emissive and non-emissive electronic transitions, and in particular spin-inversion transitions as a result of enhanced spin-orbit coupling (SOC). This article demonstrates the power of this approach by integrating carbon nanodots (CNDs) into a range of alkaline earth carbonates, sulphates, and oxalates. This is achieved using a simple, one-pot method in which the CNDs are used as crystallisation additives. Although other reports describing inorganic and hydrogen bonding-rich hosts for CDs may describe longer lifetimes and higher quantum yield, our method provides a systematic and easy approach to controlling PL properties through the selection of both the cation and anion, and the functionality of the CNDs, yielding specific fluorescence and phosphorescence colours and lifetimes. Importantly, lifetimes decrease systematically with increasing mass of the metal cation, providing a powerful demonstration of the effects of heavy atoms on SOC. That this can be achieved using biologically friendly materials such as CaCO3—where these can readily incorporate a host of guest species including proteins and drug molecules—opens the door to alternative simple-to-prepare theranostic agents.

Results

Synthesis and properties of folic acid-derived CNDs. Folic acid-derived CNDs (F-CNDs) were synthesised by thermal degradation of folic acid using a hydrothermal method. A sodium folate solution was heated at 200 °C for 12 h in an autoclave, and subsequent filtration of the resulting orange F-CND solution removed any large aggregates. Characterisation of the F-CNDs using Fourier transform infrared (FTIR) and Raman spectroscopy confirmed the presence of N-heterocycle motifs, which are retained from the folic acid precursor (Supplementary Fig. 1). These were also detected by X-ray photoelectron spectroscopy (XPS), along with ketones and carboxylate groups (Supplementary Note 1 and Supplementary Fig. 2). The latter contribute to a negative surface potential of 20 mV at pH 8. No graphitic carbon was detected by XPS (Supplementary Note 1 and Supplementary Fig. 2), or by transmission electron microscopy (TEM) (Supplementary Fig. 1), which confirmed that the nanoparticles were between 3 and 5 nm in size, and amorphous.

The photophysical properties of the F-CNDs were then investigated. Blue fluorescence was observed from aqueous solutions of F-CNDs on excitation at 365 nm (Supplementary Fig. 1). No phosphorescence was seen. F-CNDs are prone to self-quenching such that the fluorescence intensity was constant at concentrations above 1.5 × 10−4 g mL−1 (Supplementary Fig. 3). Steady-state photoluminescence (SS-PL) spectroscopy of these solutions revealed an excitation maximum at 320 nm for an emission maximum at 430 nm and 442 nm (Supplementary Fig. 4). Longer wavelength excitation (365 nm and 390 nm) yielded red-shifted emission maxima at 430 nm and 442 nm, respectively, but with significantly and progressively lower intensities (Supplementary Fig. 4).

Solutions of the F-CNDs were also analysed using fluorescence lifetime imaging microscopy (FLIM), yielding fluorescence lifetimes of τ1 = 4.81 ns (13.4% of the decay signal) and τ2 = 0.59 ns (86.6%). Dried particles exhibited shorter fluorescence lifetimes of τ1 = 1.46 ns (1.3%) and τ2 = 0.26 ns (98.7%), where the lifetime and proportion of the decay signal of the longer lifetime component were significantly reduced, and the fluorescence intensity also dropped dramatically, whereas the effect on the shorter lifetime component was proportionally weaker. Longer lifetime radiative processes are expected to be governed by electron-hole trapping by carbonyls, carboxylic acids, and N-heterocycles that are present on the surfaces of CDs and CNDs, and are therefore likely to be influenced by drying of these nanoparticles, or their integration into a solid host.

Synthesis and characterisation of F-CND/host nanocomposites. F-CND/inorganic nanocomposites were prepared by precipitating alkaline earth (Ca, Sr, and Ba) carbonate, sulphate, and oxalate crystals in the presence of F-CNDs using a simple, direct-mixing protocol. Powder X-ray diffraction (pXRD) (Supplementary Fig. 5) and Raman spectroscopy (Supplementary Fig. 6) were used to determine the structures of the product crystals, where the results are summarised in Supplementary Table 1. Scanning electron microscopy (SEM) showed that SrCO3, BaCO3, and BaC2O4·0.5H2O particles were polycrystalline and took the form of bundles of particles or spherulites (Supplementary Fig. 7), whereas the other nanocomposites precipitated as single crystals, and exhibited unmodified morphologies as compared with control experiments (Supplementary Fig. 8). The quantities of CNDs in the nanocomposite crystals were determined by dissolution of the crystals, and measurement of the fluorescence intensity of the resulting solutions. All of the inorganic particles contained 0.008 to 0.002 wt% F-CNDs. It is noted that the F-CNDs may be occluded between crystalline units in the polycrystalline samples rather than within the crystal lattice as occurs with the single crystals.
The interiors of the calcite/F-CND nanocomposite crystals were analysed using TEM, where thin sections were prepared by focussed ion beam (FIB) milling (Supplementary Fig. 9). The images were identical to sections cut through pure calcite crystals, which demonstrated that the CNDs are not aggregated within the host crystal. It is not possible to image individual amorphous CNDs as the electron beam interacts much more strongly with the crystalline host. Confirmation of the incorporation and location of the F-CNDs within their inorganic hosts was therefore obtained using confocal fluorescence microscopy (CFM). As the host phases are not luminescent (Supplementary Fig. 10), any luminescence observed derives from the F-CNDs. All polycrystals contained a uniform distribution of F-CNDs (Supplementary Fig. 7), whereas all single crystals exhibited preferential occlusion in specific zones (Fig. 1); BaSO4 crystals were too thin (~0.2–2 µm) to determine the nanoparticle location (Supplementary Fig. 7). Calcite crystals exhibited higher fluorescence intensity in one half of their volume, where this is indicative of preferential binding to the acute over the obtuse step edges (Fig. 1)\(^{24,34}\). One half of their volume, where this is indicative of preferential binding to the acute over the obtuse step edges (Fig. 1)\(^{24,34}\). Some association with the {010} faces for some association with the {010} faces for photophysical properties of F-CND/host nanocomposites. F-CND/inorganic nanocomposites exhibited SS-PL upon excitation with 365 nm UV light (Fig. 2a). The colour displayed varied between hosts, being cyan for CaCO\(_3\), blue for CaSO\(_4\)·2H\(_2\)O and green for BaSO\(_4\). While it was not possible to achieve precise control over the quantities of F-CNDs in the nanocomposites, the F-CND content could be readily controlled within a range where bright fluorescence was achieved, and where the effects of self-quenching, including reduced afterglow lifetimes and quantum yields caused by enhanced non-radiative energy loss, were minimised (Supplementary Fig. 11). As a distinct difference from F-CNDs alone, all of the nanocomposites exhibited green RTP (Fig. 2a), and SS-PL emission spectra comprised a primary peak at 398 nm, which corresponds to fluorescence, and a secondary peak at 518 nm, which corresponds to phosphorescence. Assignment of phosphorescence was made by (dark-state) spectroscopy of F-CND/SrSO\(_4\) (Supplementary Fig. 12). Notably, the relative intensity of phosphorescence to fluorescence (relative RTP intensity) increased with the cation atomic number (Z, where \(Z(Ca) < Z(Sr) < Z(Ba)\)) such that the peak appears as a shoulder to the fluorescence peak in CaCO\(_3\), but as a separate peak in SrCO\(_3\), BaCO\(_3\), SrSO\(_4\), and BaSO\(_4\) (Figs. 2b-d). This increase in relative RTP intensity is most prominent in sulphates, followed by carbonates, and is marginal in oxalates (Figs. 2a-d). Quantum yields were estimated by relating the PL intensity to the F-CND content of each nanocomposite. Fluorescence quantum yields (\(\Phi_F\)) decreased with increasing Z (CaCO\(_3\), SrCO\(_3\), and BaCO\(_3\)= 6.8, 3.2, and 0.5% respectively), whereas phosphorescence quantum yields (\(\Phi_P\)) generally increased with increasing Z (CaCO\(_3\), SrCO\(_3\), and BaCO\(_3\)= 0.3, 0.6, and 1.3%). However, the total quantum yield (\(\Phi^{\text{tot}}\)) decreased with increasing Z, suggesting enhanced quenching or non-radiative elimination of excited electronic states (Table 1).

**Photophysical properties of F-CND/host nanocomposites.** F-CND/inorganic nanocomposites exhibited SS-PL upon excitation with 365 nm UV light (Fig. 2a). The colour displayed varied between hosts, being cyan for CaCO\(_3\), blue for CaSO\(_4\)·2H\(_2\)O and green for BaSO\(_4\). While it was not possible to achieve precise control over the quantities of F-CNDs in the nanocomposites, the F-CND content could be readily controlled within a range where bright fluorescence was achieved, and where the effects of self-quenching, including reduced afterglow lifetimes and quantum yields caused by enhanced non-radiative energy loss, were minimised (Supplementary Fig. 11). As a distinct difference from F-CNDs alone, all of the nanocomposites exhibited green RTP (Fig. 2a), and SS-PL emission spectra comprised a primary peak at 398 nm, which corresponds to fluorescence, and a secondary peak at 518 nm, which corresponds to phosphorescence. Assignment of phosphorescence was made by (dark-state) spectroscopy of F-CND/SrSO\(_4\) (Supplementary Fig. 12). Notably, the relative intensity of phosphorescence to fluorescence (relative RTP intensity) increased with the cation atomic number (Z, where \(Z(Ca) < Z(Sr) < Z(Ba)\)) such that the peak appears as a shoulder to the fluorescence peak in CaCO\(_3\), but as a separate peak in SrCO\(_3\), BaCO\(_3\), SrSO\(_4\), and BaSO\(_4\) (Figs. 2b-d). This increase in relative RTP intensity is most prominent in sulphates, followed by carbonates, and is marginal in oxalates (Figs. 2a-d). Quantum yields were estimated by relating the PL intensity to the F-CND content of each nanocomposite. Fluorescence quantum yields (\(\Phi_F\)) decreased with increasing Z (CaCO\(_3\), SrCO\(_3\), and BaCO\(_3\)= 6.8, 3.2, and 0.5% respectively), whereas phosphorescence quantum yields (\(\Phi_P\)) generally increased with increasing Z (CaCO\(_3\), SrCO\(_3\), and BaCO\(_3\)= 0.3, 0.6, and 1.3%). However, the total quantum yield (\(\Phi^{\text{tot}}\)) decreased with increasing Z, suggesting enhanced quenching or non-radiative elimination of excited electronic states (Table 1).

![Fig. 1](https://www.nature.com/naturecommunications)

**Fig. 1** Visualising the integration of folic acid-derived carbon nanodots (F-CNDs) in inorganic single crystals. Optical microscopy images (a–e), confocal fluorescence microscopy (CFM) images (f–j), and distribution models (k–o) of CaCO\(_3\) (a, f, k), CaSO\(_4\)·2H\(_2\)O (b, g, l), SrSO\(_4\) (c, h, l), CaC\(_2\)O\(_4\)·H\(_2\)O (d, i, n), and SrC\(_2\)O\(_4\)·H\(_2\)O (e, j, o). All CFM images have accompanying look-up table (LUT) scales signifying PL intensity, from white (max) to cyan to blue to black (zero). Scale bars: 20 µm (a, c, f, h), 150 µm (b, g), 5 µm (d, i) and 10 µm (e, j).
The PL lifetimes of the F-CNDs also varied according to the composition of the inorganic host. The fluorescence lifetimes (both $\tau_1^F$ and $\tau_2^F$) of the F-CNDs embedded in all inorganic hosts were shorter than in aqueous solutions. Increasing the cation Z resulted in a decrease in the value and proportion of the longer ($\tau_1^F$) lifetime (Table 1 and Figs. 3c, d). The shorter ($\tau_2^F$) lifetime, however, did not change proportionally with Z, suggesting a different trend (Supplementary Fig. 13). RTP decay curves were obtained from video stroboscopic studies (excitation at 365 nm at 40 ms intervals) (Figs. 2e-h), and these were fitted with a single exponential function, yielding RTP lifetimes ($\tau_P$) of 127 ms, 110 ms, and 72 ms for CaCO$_3$, SrCO$_3$, and BaCO$_3$, respectively (Table 1 and Figs. 3e, f). This indicates that $\tau_P$ also decreases with increasing cation Z. The sulphates and oxalates also followed this trend (Fig. 3e).

Time-resolved phosphorescence microscopy (TRPM; 40 $\mu$W excitation at 340 nm at 5 ms intervals) was additionally used to examine the afterglow, and to confirm that the RTP originated from individual particles. RTP decay plots were fitted with a triple exponential function, yielding three lifetimes of $\tau_1^P = 102.7$ ms (50.7%), $\tau_2^P = 34.0$ ms (40.7%), and $\tau_3^P = 2.9$ ms (9.1%) for calcite (Table 1 and Supplementary Fig. 13). This shows that the RTP...
behaviour is complex and originates from various relaxation events in the F-CNDs. These lifetimes are shorter than those determined from video stroboscopy due to differences in excitation intensities and wavelengths, but the same trend with respect to the host cation Z is observed (Supplementary Fig. 13).

**Table 1 Physical and PL properties of F-CND/host nanocomposites**

| Mineral host                     | Density (g cm−3) | Relative RTP intensitya | φF (%) | φP (%) | φtot (%) | τF (ns) | τP (ms) | τF b (ms) | τP c (ms) | τF c (ms) | aP c (%) | aP f (%) | aP c (%) | aP f (%) |
|----------------------------------|------------------|-------------------------|--------|--------|----------|--------|--------|----------|----------|----------|----------|----------|----------|----------|
| Mg3(CO3)2(OH)2·4H2O             | 2.25             | 0.03                    | 8.6    | <0.1   | 8.6      | 3.45   | 0.47   | 5.6      | 94.4     | ND       | 114.9    | 23.4    | 3.6      | 22.9    |
| CaCO3 (Calcite)                 | 2.71             | 0.13                    | 6.8    | 0.3    | 7.1      | 3.27   | 0.56   | 11.0     | 89.0     | 127.7    | 34.0    | 2.9      | 50.2    | 40.7    |
| SrCO3                           | 3.78             | 0.22                    | 3.2    | 0.6    | 3.8      | 2.76   | 0.46   | 6.6      | 93.4     | 110.0    | 82.3    | 26.1    | 53.6    | 23.2    |
| BaCO3                           | 4.3              | 0.84                    | 0.5    | 1.3    | 1.8      | 2.26   | 0.39   | 3.2      | 96.8     | 72.0     | 54.7    | 26.7    | 7.9      | 28.9    |
| Pb3(CO3)2(OH)2                  | 6.5              | >0.99                   | 0.0    | <0.1   | <0.1     | 1.42   | 0.21   | 0.3      | 99.7     | ND       | 3.6     | 0.4     | ND      | NA      |
| CaCO3 (amorphous)               | 1.62             | 0.03                    | NC     | NC     | NC       | 2.90   | 0.46   | 7.5      | 92.5     | 130.0    | 104.0   | 35.6    | 6.7      | 41.3    |
| CaCO3 (vaterite)                | 2.65             | 0.08ab                  | NC     | NC     | NC       | ND     | ND     | ND       | ND       | ND       | ND      | ND      | ND      | ND      |
| CaSO4·2H2O                      | 2.31             | 0.13                    | 7.2    | 0.6    | 7.8      | 2.14   | 0.31   | 1.0      | 99.0     | 121.5    | 111.5   | 33.3    | 3.9      | 50.1    |
| SrSO4                           | 3.95             | 0.72                    | 1.7    | 2.9    | 4.6      | 2.13   | 0.37   | 3.6      | 96.4     | 90.0     | 82.4    | 32.8    | 7.1      | 38.1    |
| BaSO4                           | 4.48             | 0.98                    | 0.0    | 2.2    | 2.2      | 1.38   | 0.25   | 0.9      | 99.1     | 73.0     | 48.7    | 19.9    | 3.9      | 38.9    |
| CaC2O4·H2O                      | 2.21             | 0.09                    | 2.7    | 0.1    | 2.8      | 3.33   | 0.52   | 7.6      | 92.4     | 128.0    | ND      | ND      | ND      | ND      |
| SrC2O4·H2O                      | 2.85             | 0.18                    | 0.3    | <0.1   | 0.3      | 2.66   | 0.58   | 7.2      | 92.8     | 105.0    | ND      | ND      | ND      | ND      |
| BaC2O4·0.5H2O                   | 3.45             | 0.28                    | 0.6    | 0.4    | 1.0      | 1.99   | 0.25   | 10.3     | 89.7     | 82.0     | 57.6    | 20.8    | 6.2      | 28.1    |
| FolicoCD (aqueous solution)      | NA               | ND                      | ND     | ND     | ND       | ND     | ND     | ND       | ND       | ND       | ND      | ND      | ND      | ND      |
| FolicoCD (dried from solution)   | NA               | ND                      | ND     | ND     | ND       | ND     | ND     | ND       | ND       | ND       | ND      | ND      | ND      | ND      |

Tabulated data of density, relative RTP intensity, and fluorescence and phosphorescence quantum yields (Φ), lifetimes (τ), and pre-exponential factors (α) (ND not detected, NA not applicable, NC Not calculated, F-CND folic acid-derived carbon nanodot, PL photoluminescence, RTP room temperature phosphorescence, SS-PL steady-state photoluminescence, TRPM time-resolved phosphorescence microscopy, PLM phosphorescence lifetime imaging microscopy)

aRelative RTP intensity is estimated from SS-PL spectroscopy
bFrom video stroboscopy studies
cTaken from TRPM studies
dFrom PLM data

**Discussion**

These experiments show that PL behaviour in RTP F-CND/host nanocomposites can be tuned through judicious selection of the inorganic host. Our data show that all fluorescence and...
phosphorescence quantum yields, lifetimes and relative intensities are related to host cation Z (Table 1). The condensed host phase forces cations close to the F-CND surface, and heavier atoms interfere with electronic transitions (internal conversion (IC), intersystem crossing (ISC), fluorescence, and phosphorescence) within the photoactive carbonyl and N-heterocycles F-CND surface groups (Fig. 5). Each transition has an associated rate constant (i.e., $k_{IC}$, $k_{ISC}$, $k_{IC}$, and $k_{P}$), which increases with Z, ultimately leading to fluorescence quenching and RTP activation.

Fluorescence quenching is caused by increased $k_{IC}$ and $k_{ISC}$, which depopulate the excited singlet state non-radiatively, and increased $k_{F}$ leads to shortened fluorescence lifetimes. This is known as the Kasha effect, where heavy atoms interfere with electron-hole recombination in luminophores. RTP activation is due to enhanced ISC as $k_{SC}$ increases, where this populates the first excited triplet state, as is necessary for phosphorescence. ISC is a forbidden spin-inversion process, which is facilitated through SOC, a phenomenon that effectively mixes singlet and triplet character. This is enhanced with both increasing Z and decreasing distance between the heavy atom and the electron undergoing spin inversion, in the well-known heavy atom effect. Phosphorescence, which is also a spin-inversion process, is therefore similarly enhanced, leading to a higher rate of relaxation ($k_{P}$) to the ground singlet state and a shorter observed lifetime as observed in our study with increasing Z. Also, although $\Phi_{tot}$ increased with Z, $\Phi_{ttr}^{s}$ decreased significantly with Z, which is a result of enhanced radiationless ISC ($k_{IS}^{s}$). This competes against other electronic transitions, and effectively quenches the net luminescence.

Further insight into the relationship between Z and RTP was gained by examining hosts with lighter (Mg, $Z = 12$) and heavier (Pb, $Z = 82$) metals. Hydromagnesite (Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O) and hydrocerrusite (Pb$_3$(CO$_3$)$_2$(OH)$_2$) were precipitated from aqueous solution in the presence of F-CNDs (Supplementary Fig. 17). Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O fluoresced blue under UV excitation, and produced a very weak green afterglow (Table 1). The SS-PL emission spectrum featured a single phosphorescence peak, which was red-shifted compared to F-CND/CaCO$_3$, signifying a lower relative RTP intensity (Fig. 6) and a much smaller $\Phi_{tot}$ than for calcite. Similarly, TRPM indicates a longer RTP lifetime of 0.4 ms (Table 1). The SS-PL spectrum featured a single phosphorescence peak, which was red-shifted compared to F-CND/CaCO$_3$, signifying a lower relative RTP intensity (Fig. 6) and a much smaller $\Phi_{tot}$ than for calcite. Similarly, TRPM indicates a longer RTP lifetime of 0.4 ms (Table 1).
shifted as compared with F-CND/BaCO₃ nanocomposites (Supplementary Fig. 17). A much lower quantum yield (Table 1), and a significantly shorter lifetime suggests that the very high Z of Pb causes a disproportionate increase in $k_{SC}$ compared with $k_{ISC}$.

The quantum yields, relative RTP intensity, and lifetimes are also influenced by the anion present. This can be related to two effects. First, F-CND/oxalate nanocomposites have much lower quantum yields than the corresponding carbonates and sulphates, which suggests that the oxalate anion may enhance $k_{SC}$—
containing different anions have different densities ($\rho$) and therefore greater RTP activation.

For a given cation, cation of the same Z should therefore result in a shorter r.

The effects of increasing Z on rate constants is summarised in Table 2. As Z increases...

Finally, our synthetic strategy provides a unique opportunity to create materials with specific PL properties. By simply creating different cation hosts—where it is possible to tune the elemental composition of the simple inorganics employed here over a wide range—one can systematically control the average atomic mass and density of the host environment. This strategy was demonstrated here with Sr/BaCO$_3$ and Sr/CaCO$_3$ solid solutions as hosts for F-CNDs (Fig. 7). Mixed metal carbonates were precipitated from solutions containing different ratios of CaCl$_2$, SrCl$_2$, and BaCl$_2$, and defined concentrations of Na$_2$CO$_3$ and F-CND (Supplementary Table 2), and their compositions were determined using XRD (Fig. 7b). All of the product crystals produced RTP after UV excitation (Fig. 7a). Normalised fluorescence spectra (Supplementary Fig. 18) revealed the anticipated progressive increase in relative RTP intensity with increasing average Z (Fig. 7c) while RTP lifetimes decreased with increasing Z (Fig. 7d). Quantum yields determined from absolute PL intensities exhibited a progressive decrease in $\Phi^F$, an increase in $\Phi^P$, and a significant decrease in $\Phi^{450}$ with increasing Z (Fig. 7e). These demonstrate that subtle, controllable changes in the host

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**Fig. 5** The mechanism for PL behaviour modification in carbon nanodot (CND)/host nanocomposites. Modified Jablonski diagram indicating electronic states ($S_0$ (black), $S_1$ (blue), and $T_1$ (green)) and their relative energy levels; electronic transitions (non-emissive absorption (dotted purple), intersystem crossed (ISC, dotted black), internal conversion (IC, dotted black), and thermal relaxations (jagged black); and emissive fluorescence (solid blue) and phosphorescence (solid green)) and associated rate constants; and electronic spin states ($S_0$, $S_1$, and $T_1$). The effect of increasing Z on rate constants is summarised in Table 2. As Z increases...

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The implications of increasing Z on fluorescence and phosphorescence intensities (b) and lifetimes (c) are summarised with photoluminescent (PL) spectra (b) and decay curves (c). PL spectra and decay curves are given in greyscale, from low Z (white) to high Z (black).

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Oxalate host phases also contain structural water, which may influence RTP activation. However, as bright luminescence and RTP activation occurs in water-containing CaSO$_4$·2H$_2$O and ACC (CaCO$_3$·H$_2$O) nanocomposites (Figs. 2 and 4), as well as the water-rich KAl(SO$_4$)$_2$·12H$_2$O$_{19}$ and cyanuric acid-based hosts$_{31}$, the large reduction in $\Phi^{60}$ in oxalate-based hosts is attributed to the oxalate ion itself. It is proposed that the structural water has a passive role, neither actively promoting nor quenching RTP, but causing a decrease in the density of the host crystal when present. This change in the host’s physical properties then influences the RTP behaviour. Second, hosts containing different anions have different densities ($\rho$). The magnitude of SOC is roughly proportional to the fourth power of Z, and also the inverse cube of distance (r) between the perturbed electron and perturbing nucleus. A denser phase with a higher Z, and also the inverse cube of distance ($\rho r^3$) and associated rate constants; and electronic spin states ($S_0$, $S_1$, and $T_1$). The effect of increasing Z on rate constants is summarised in Table 2. As Z increases...

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Oxalate host phases also contain structural water, which may influence RTP activation. However, as bright luminescence and RTP activation occurs in water-containing CaSO$_4$·2H$_2$O and ACC (CaCO$_3$·H$_2$O) nanocomposites (Figs. 2 and 4), as well as the water-rich KAl(SO$_4$)$_2$·12H$_2$O$_{19}$ and cyanuric acid-based hosts$_{31}$, the large reduction in $\Phi^{60}$ in oxalate-based hosts is attributed to the oxalate ion itself. It is proposed that the structural water has a passive role, neither actively promoting nor quenching RTP, but causing a decrease in the density of the host crystal when present. This change in the host’s physical properties then influences the RTP behaviour. Second, hosts containing different anions have different densities ($\rho$). The magnitude of SOC is roughly proportional to the fourth power of Z, and also the inverse cube of distance (r) between the perturbed electron and perturbing nucleus. A denser phase with a higher Z, and also the inverse cube of distance ($\rho r^3$) and associated rate constants; and electronic spin states ($S_0$, $S_1$, and $T_1$). The effect of increasing Z on rate constants is summarised in Table 2. As Z increases...

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The implications of increasing Z on fluorescence and phosphorescence intensities (b) and lifetimes (c) are summarised with photoluminescent (PL) spectra (b) and decay curves (c). PL spectra and decay curves are given in greyscale, from low Z (white) to high Z (black).

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materials, such as electroluminescent, catalytic and light-harvesting materials, where a high degree of control over electronic properties is essential.

**Methods**

**Materials.** Folic acid, calcium carbonate, calcium chloride dihydrate, strontium chloride hexahydrate, barium chloride, magnesium chloride hexahydrate, sodium carbonate, sodium sulphate, riboflavin, fluorescein sodium salt, dextran (Sigma-Aldrich, UK); lead nitrate, 13% sodium hypochlorite solution, and sodium hydroxide (Fisher, UK) were used as purchased, without further purification. Deionised (DI) water was obtained from an in-house Millipore Reference A+ water purification system (MilliQ, 1–2 ppm OC, 18.2 MΩ).

**CND synthesis.** In all, 0.1 g folic acid was added to 20 mL DI water and stirred for 20 min yielding a yellow suspension. Under constant stirring, 3 M aqueous NaOH solution was added dropwise to the suspension, resulting in dissolution of folic acid to sodium folate in a yellow solution. The pH of the final solution was 6.0–6.1. The solution was added to a 40 mL stainless steel hydrothermal autoclave with a Teflon insert and sealed. The autoclave was placed in an oven preheated to 200 °C and heated for 12 h. After the oven cooled down to room temperature naturally, the orange/yellow product solution was filtered using a syringe-driven 0.22 μm pore size Millipore polycarbonate filter to remove large particles/aggregates. F-CND powders were obtained by lyophilisation and stored in a desiccator, or used from solution as prepared. For R-CNDs, the same protocol was repeated except folic acid was replaced with riboflavin. All other aspects were identical.

**Cation/anion stock solution preparation.** All stocks were prepared by adding 20 mL DI water to a calculated amount of solid in a clean 28 mL vial capped with a plastic lid as shown in Supplementary Table 3, and stirred until all powder was fully dissolved. Solutions were filtered before use through a syringe-driven 0.22 μm pore size Millipore polycarbonate filter. Although most of these stock solutions were stable for a few weeks if correctly stored and sealed, Na2CO3 and NaHCO3 stock solutions were made fresh before each experiment.

**Crystal growth.** In all experiments, 20 mL Petri dish and 400 mL glass beaker reaction vessels were cleaned in a base bath (1 M KOH in iPrOH), rinsed in an acid bath (1 M HCl in H2O), then rinsed with DI water and dried in a 60 °C oven for at least 2 h before use. In total, 25 mL glass vials were used as received. Each reaction vessel was charged with a Piranha solution-cleaned glass substrate before crystallisation. R-CNDs were bleached by heating the glass slide was removed and rinsed with excess DI water, followed by ethanol, and allowed to dry.

The remaining CND/calcite composite single crystals on the surface of the Petri dish were obtained by careful disposal of the crystallisation liquor, followed by rinsing with excess DI water and ethanol. Then, a small amount (≤ 0.5 mL) of ethanol was added into the Petri dish, and the crystals were agitated from the glass surface using a spatula. When liberated from the surface and free-floowing in suspension, the crystals were collected from the ethanol by vacuum-driven filtration using a Millipore filtration system and a 0.45 μm polycarbonate membrane. The dried powder was then added to 2 mL 13% sodium hypochlorite solution in a 15 mL glass vial and left for 5 min. After bleaching, the bleach was carefully removed from the vial using a pipette, and carefully disposed. The bleached crystals were then carefully rinsed with excess water and filtered using the Millipore filtration system. Extra washing with DI water and ethanol took place in the filtration system itself. This protocol can be easily adapted for any of the target devices by making appropriate adjustments to the conditions, reaction vessels, concentrations, volumes, and salts by following the instruction in Supplementary Table 4.

**Composition and properties.** Time-resolved phosphorescence microscopy images with UV excitation (a) on and (b) 5 ms after the removal of UV excitation, and (c) intensity vs time plots for calcite (black square) and vaterite (brown triangle)-based RTP nanocomposites. The plot in (c) shows the intensity with UV light on and off, and the point at which the light is removed is shown with a vertical red line at t = 0. The normalised decay curves for calcite and vaterite overlap, indicating identical phosphorescent lifetimes (inset; scale bar 50 μm).

Fig. 6 Dependence of room temperature phosphorescence activation on the crystal phase. Time-resolved phosphorescence microscopy images with UV excitation (a) on and (b) 5 ms after the removal of UV excitation, and (c) intensity vs time plots for calcite (black square) and vaterite (brown triangle)-based RTP nanocomposites. The plot in (c) shows the intensity with UV light on and off, and the point at which the light is removed is shown with a vertical red line at t = 0. The normalised decay curves for calcite and vaterite overlap, indicating identical phosphorescent lifetimes (inset; scale bar 50 μm).
Fluorescence quantum yields decrease with Z, whereas phosphorescence/RTP quantum yields increase with Z. Overall, the total quantum yield falls.

Photographs with, and immediately after the removal of, UV (365 nm) excitation of F-CND nanocomposites with different Ca/Sr/BaCO₃ solid solutions are shown in Fig. 7. X-ray diffraction (XRD) patterns in the range 2θ = 23–27° of samples, where the peak centre for [111] reflection is shown to move to a smaller angle with an increasing average Z of the host. Relative room temperature phosphorescence (RTP) intensity values obtained from background-subtracted normalised SS-PL spectra showing the progressive activation of RTP with increasing Z. Lifetime measurements obtained by video stroboscopy showing shorter lifetimes as Z increases.

Fluorescence quantum yields decrease with Z, whereas phosphorescence/RTP quantum yields increase with Z. Overall, the total quantum yield falls.

**ACC synthesis.** A Millipore vacuum-driven filtration system with a 0.45 μm pore size polycarbonate membrane was prepared before the reaction by running approx. 20 mL ethanol through the filter. The vacuum was kept on, while the ACC was prepared. In all cases, 200 μL F-CND solution was mixed with 2.5 mL 200 mM CaCl₂ aqueous solution in a 5 mL centrifuge tube. Then, 2.5 mL 200 mM Na₂CO₃ solution was added rapidly, before the centrifuge was closed and shaken vigorously for 5 s. The gel-like suspension was then poured into the filtration system, and the water drawn away immediately. The centrifuge tube and the retained F-CND/ACC composite was washed with ethanol. The composite was allowed to dry, and was then stored over dried silica desiccant. Due to the sensitivity to moisture, samples were only removed immediately before analysis.

**Calcite nanoparticle synthesis.** In all experiments, 50 mL DI water was degassed/decarbonated by refluxing at 80 °C in a three-necked round bottom flask under N₂ flow for 6 h. In total, 0.44 g CaO, formed by calcination of pure CaCO₃ at 900 °C for 8 h, was added, and stirring, heating, and N₂ bubbling was continued for 15 min to facilitate Ca(OH)₂ formation. The solution was aged in the closed, sealed vessel at room temperature for 16 h. In all, 2 mL F-CND solution was then mixed with aged Ca(OH)₂ for 10 min. The solution was carbonated by bubbling a 3:1 mixture N₂/CO₂ through the solution at an overall flow rate of 1 L min⁻¹ under stirring at room temperature. The reaction progress was monitored by pH, such that the reaction was stopped when pH = 7 by removing gas supply and closing the system. Dry, clean nanoparticles were obtained by centrifugation and twice washing with ethanol, before suspension in sodium hypochlorite (5%) solution for 2 h and further centrifugation and drying steps.

**Raman microscopy and spectroscopy.** Raman microscopy was conducted on inorganic CND/host nanocomposites grown on glass substrates using a Renishaw inVia Raman Microscope (785 nm laser) with a 50× objective using MS20 encoded sample stage control through rollerball XYZ peripheral. Data acquisition was undertaken with Renishaw WiRE 3.4 with a laser intensity of 0.1% under three accumulations (3 × scan time 30 s) between 1200 and 100 cm⁻¹. Raman spectroscopy of CNDs was conducted using a Renishaw inVia Raman confocal inverted microscope integrated with a Leica DMi8/SP8 laser scanning confocal microscope system, with a 785 nm diode laser (laser power of 4.5 mW on the sample, intensity of ~5.7 × 10⁹ W cm⁻²) and a 12001 mm⁻¹ grating. Light was collected using a near infrared enhanced CCD array detector (1024 × 256 pixels). Prior to every experiment, a spectrum of a silicon sample was collected and the microscope was calibrated to the peak position (520.5 cm⁻¹). The sample was drop cast onto a quartz slide from an aqueous suspension and dried under nitrogen. Spectra were collected with a 40× objective (NA 0.85 HCX PL APO CORR CS) acquiring for 200 s. Baseline subtraction was done using the Matlab function fBaseline_corr with bandwidth of 350, smoothwidth of 30 and 20 iterations⁵⁰. Spectra were analysed with reference to Raman spectra of folic acid⁵¹ and riboflavin⁵².

**pXRD.** pXRD was conducted using a Bruker D2 Phaser with a LYNXEYE detector for phase confirmation studies. Dry powdered samples were deposited onto a silicon substrate as dried powder or from ethanolic suspension. Data were obtained between 2θ = 5 and 95° over 20 min, with the smallest possible step size, on spinning samples. All data acquisition, instrument control, and data conversion were conducted in DIFFRAC.SUITE software package.
SEM. SEM was conducted using an FEI NanoSEM Nova 450 of samples grown directly on clean glass substrates. Samples were mounted on aluminum stubs with double sided Cu tape, with tape folded to a portion of the top surface of the substrate to minimise charging. All samples were coated with 2 nm Ir conductive layer prior to analysis.

Analysis of the CND content of the nanocomposites. A known mass of each nanocomposite was dissolved in a known volume of HCl/EDTA (approx. 2% HCl, 150 mM Na2EDTA). The concentration of the CNDs in solution was then determined by comparing the fluorescence intensity (obtained on a Perkin-Elmer Envision 2103, λem = 320 nm, λex = 405 nm) against a calibration curve prepared from known masses of CNDs in the same solvent. These data were then employed to calculate the wt% of CNDs in the nanocomposites.

CFM. CFM was conducted using a Zeiss LSM510 Upright Confocal Microscope of samples grown directly on clean glass substrates under oil immersion where required. Laser and imaging settings were controlled with Zeiss ZEN software (excitation laser at 405 nm, emission low pass filter from 440 nm).

Image analysis. For all confocal fluorescence and SEM micrographs, rendering and analysis was conducted in ImageJ or Fiji applet. For CFM z-stacks, optical images were taken from the central most plane. Fluorescence confocal micrographs were obtained by forming a z-projection for z-stacks. Surface images, as viewed from various angles, were obtained by rendering confocal fluorescence z-stacks into 3D, and rotating the rendered image manually.

SS-PL spectroscopy. SS-PL (spectroscopy) (excitation and emission) were obtained from diluted CND solution and solid powders using a Jobin Yvon Horiba FluoroMax-3 fluorescence spectrometer operated by FluorEssence (v3.5) software. Powdered samples were prepared for fluorescence spectroscopy in two methods, depending on the required analysis. For relative RFP intensity calculations, nanocomposite samples were mixed with grease and smeared onto a glass substrate. PL spectra of grease and glass slide were used as background signals. For absolute intensity measurements and quantum yield estimates, nanocomposite samples were pulv- erised with a pestle and mortar, then pelletised with a piston-driven IR press at 7 measurements and quantum yield estimates, nanocomposite samples were pulv- erised and glass slide were used as background signals. Absolute intensity measurements and quantum yield estimates, nanocomposite samples were pulv- erised with a pestle and mortar, then pelletised with a piston-driven IR press at 7 measurements.

Phosphorescence spectroscopy. Phosphorescence (dark-state) spectra were obtained using Ocean Optics 2000− interferencing fibre optic signal inlet to a Sony ILX511B CCD detector with Overture (v1.0.1) software control. Powdered samples were prepared as above, and excited with an Applied Photophysics 150 W shut- tered xenon arc lamp. Excitation light (360 nm) was filtered with a Comar Optics 360−50 band pass filter (bandwidth between 300 and 400 nm, asymmetric transmittance peak centred on 360 nm).

UV-Visible (UV-Vis) absorbance spectroscopy. Absorption spectra of aqueous CND solutions were obtained on a Perkin-Elmer Lambda 35 spectrometer in a quartz cuvette, with a 1 cm path length. Spectra were obtained between 200 nm at 240 nm min−1, with 1 nm intervals. Data acquisition, instrument control, and automatic background deletion were handled by the UV WinLab software.

FTIR spectroscopy. FTIR spectra were obtained with Perkin-Elmer Spectrum 100 with ATR accessory and sample mounting. Spectra were obtained across 650 to 4000 cm−1 at 1 cm−1 intervals, accumulated over four runs. Data acquisition, instrument control, and automatic background deletion were handled by the Spectrum software.

Zeta potential determination. Zeta potential measurements were obtained using a Malvern Instruments Zetasizer Nano from samples prepared in a Zetasizer Nano disposable capillary cell. All data were obtained on diluted samples, typically over 20 accumulations, and run six times to ensure agreement of data. Data acquisition, instrument control, data analysis, and conversion were conducted with the Zeta- sizer family software package (v7). Note that fluorescent, coloured samples are not ideal for zeta potential/dynamic light scattering studies.

Video stroboscopy. Videos of RTP composites were obtained with a Canon EOS 7D SRL camera in video mode (25 fps) with manual focus and manual exposure settings; with a Canon EF 100 mm f/2.8 Macro USM lens. Photoluminescence was stimulated with a Spectroline UV lamp (6 W longwave 365 nm), and shuttered manually. Video sequencing was conducted using InterMicroscopy 10.4 (64-bit) for frame isolation and image sequence generation, followed by image analysis and recom- position in ImageJ 1.46r. These videos were used for low-resolution stroboscopy.

Fluorescence and phosphorescence quantum yield calculations. The quantum yield of an aqueous solution of F-CNDs was estimated by comparing the luminescence intensity of known particle/molecular concentrations against fluorescein sodium salt solutions. SS-PL data were obtained at λexc = 365 nm with slits at 1 nm, while the emission quantum yield of fluorescein was calculated as 11.3%. The relative absorbance/excitation for F-CND at 365 nm was ≈ 0.07 of that at the excitation maximum at 320 nm, and this was factored into quantum yield estimate (Sup- plementary Fig. 1).

TEM. TEM was conducted using an FEI Tecnai TF20 FEG-TEM fitted with an Oxford Instruments INCA 350 EDX system/80 mm X-Max SDD detector and a Gatan Orius SC600A CCD camera operating at 200 kV. Samples were loaded onto carbon-coated Cu grids.

FIB lithography. Glass substrates loaded with calcite grown in the presence of CNDs were adhered to an aluminium SEM sample holder using silver paint. Milling was performed using a FEI Helios G4 CX FEG SEM instrument equipped with a FIB. The operating voltage was 30 kV and the beam current was varied between 0.1 and 5 nA. All samples were coated in a thick layer of platinum prior to milling to protect the sample where milling was not required.
Quantum yields of F-CND/host nanocomposite solids were estimated by comparing their luminescence (fluorescence and phosphorescence) intensity with fluorescein/CaCO₃ mixtures. Particle per unit volume was calculated for all samples. Samples were finely ground, and then pelleted as above. Background-subtracted SS-PL for each sample were used to obtain fluorescence intensities and phosphorescence intensities (and therefore total PL intensities). Phosphorescence intensities were calculated by subtracting a fitted fluorescence peak from the spectrum. These values were compared with luminescence intensities of fluorescein at equivalent concentrations to obtain a quantum yield estimate. Quantum yields were estimated assuming a single absorption/emission event occurred per particle.

Data availability

Data (PL, FTIR, Raman, and UV-Vis spectra; FLIM/PLIM images; pXRD patterns; and TRPM and stroboscopy videos) that supports the findings of this study are available in the Research Data Leeds Repository with the identifier [http://dx.doi.org/10.5518/371].

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Author contributions
F.C.M. ran the project. D.C.G. designed and conducted all experiments and analysis unless otherwise stated. A.W. and S.W.B. designed and supported FLIM/PLIM and TRPM experiments. D.C.G., M.A.H., M.A.L., and S.Z. ran FLIM/PLIM and TRPM studies. B.R.G.J., J.Gd.P., and D.C.G. supported and ran XPS and Raman studies on CNDs, and analysed the data. D.C.G. and F.C.M. wrote the paper with contributions from all authors.

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