Carbon dots in zeolites: A new class of thermally activated delayed fluorescence materials with ultralong lifetimes

Jiancong Liu, Ning Wang, Yue Yu, Yan Yan, Hongyue Zhang, Jiyang Li*, Jihong Yu*

Thermally activated delayed fluorescence (TADF) materials are inspiring intensive research in optoelectronic applications. To date, most of the TADF materials are limited to metal-organic complexes and organic molecules with lifetimes of several microseconds/milliseconds that are sensitive to oxygen. We report a facial and general "dots-in-zeolites" strategy to in situ confine carbon dots (CDs) in zeolitic matrices during hydrothermal/solvothermal crystallization to generate high-efficient TADF materials with ultralong lifetimes. The resultant CDs@zeolite composites exhibit high quantum yields up to 52.14% and ultralong lifetimes up to 350 ms at ambient temperature and atmosphere. This intriguing TADF phenomenon is due to the fact that nanoconfined space of zeolites can efficiently stabilize the triplet states of CDs, thus enabling the reverse intersystem crossing process for TADF. Meanwhile, zeolite frameworks can also hinder oxygen quenching to present TADF behavior at air atmosphere. This design concept introduces a new perspective to develop materials with unique TADF performance and various novel delayed fluorescence-based applications.

INTRODUCTION

Materials with long-lived excited states, such as phosphorescence or thermally activated delayed fluorescence (TADF) materials, have aroused considerable interest for their important applications in optoelectronics, photocatalytic reactions, molecular imaging, and security aspects (1–4). In particular, the TADF materials have the ability to harvest triplet excited states for the highly efficient reverse intersystem crossing (RISC) from triplet (T1) to singlet (S1) excited states, thus exhibiting high quantum efficiency and unique optoelectronic properties (5–8). These materials are finding great use in organic light-emitting diodes (OLED) and sensors (9–11). To date, most of the reported TADF materials are based on metal-organic complexes (for example, Cu(I), Ag(I), and Au(I) complexes (12)) and organic molecules (for example, organic donor-acceptor molecules (13, 14) and fullerenes (15)) with the lifetimes limited in the range of several microseconds to several milliseconds (16–19). Moreover, most of them display TADF behaviors in the absence of oxygen because oxygen is a strong quencher of the triplet state emission (20). New TADF materials with ultralong lifetimes at ambient conditions are highly desired to promote the multifunctional applications of TADF materials. Because triplet excitons are easily deactivated by nonradiative decay processes derived from the vibration and rotation of emitters and host molecules, energy transfer to other molecules, or triplet-triplet annihilation of emitters, to effectively suppress the nonradiative decay processes is crucial to achieve the long-lived excited states for TADF materials.

In recent years, carbon dots (CDs) as new emerging luminescent nanoparticles have received extensive attraction because of their low toxicity, biocompatibility, photostability, and photoluminescent properties (21–24). Notably, a new kind of room temperature phosphorescent material has been prepared by incorporating CDs into the matrices of polyvinyl alcohol (25, 26), potash alum (27), and polyurethane (28). The matrices can restrict the intramolecular vibrations and rotations of the functional groups on CDs, thus stabilizing the triplet excited states. Note that the TADF emission with a slow decay lifetime of 676 to 810 ns can be observed in water-soluble CDs from 100 to 250 K in which the frozen solution acts as a rigid matrix to suppress the nonradiative relaxation of CDs and thus promotes the TADF behavior (29). Finding a more suitable host matrix with a strong ability to harvest triplet excited states and generating a new class of CD-based materials having unique TADF properties at ambient conditions would be of great interest. Ordered nanoporous materials with well-confined spaces, especially zeolites with high thermal and chemical stability, are ideal candidates to incorporate functional guests (30–35). Generally, the direct in situ incorporation of photoluminescent materials into inorganic porous materials requires a strong driving force for the assembly of guest luminescent species and host inorganic frameworks (36–38). Fortunately, the hydrothermal or solvothermal synthetic conditions for zeolites are suitable for CDs, in which the organic amines and solvents can provide the raw materials for the formation of CDs (39). Therefore, the in situ incorporation of CDs into zeolite crystals under hydrothermal or solvothermal conditions to produce CDs@zeolite composites is highly possible.

Here, a facile and general strategy has been developed to synthesize a new class of CD-based TADF materials with ultralong lifetimes by in situ embedding CDs within a series of zeolitic crystalline matrices under solvothermal/hydrothermal conditions (Fig. 1). The CDs@zeolite composites with high quantum yields (QYs) up to 52.14% and ultralong TADF lifetimes up to 350 ms at ambient temperature and atmosphere have been successfully prepared. By varying the synthetic conditions of zeolitic compounds, such as the organic structure-directing agents (SDAs) and the solvents, the CDs@zeolite composites with modulated QYs and lifetimes can be synthesized. A possible mechanism for the formation of these CD-based TADF materials has been proposed, and their application in dual-mode security protection has been demonstrated. This work provides a new “dots-in-zeolites” protocol for the design and preparation of novel TADF materials and may thus open various delayed fluorescence-based applications in solar cells, high-resolution bioimaging, sensing, and security protection.

RESULTS AND DISCUSSION

Synthesis of CDs@zeolite composites

Taking aluminophosphate zeolite AlPO-5 (AIF) as an example, we have demonstrated an in situ method to prepare CDs@zeolite TADF materials...
Fig. 1. Proposed in situ formation process of photoluminescent CDs@AlPO-5 composite. The reaction mixture is composed of inorganic precursors and organic species. Under the solvothermal condition, the formation of CDs is accompanied with the crystallization of zeolite, and the CDs can be in situ embedded and confined in the zeolite matrix during the crystal growth, resulting in photoluminescent CDs@zeolite composite.

Fig. 2. SEM and TEM images and photoluminescence properties of CDs@zeolite composites. (A) Scanning electron microscopy (SEM) image of CDs@AlPO-5 composite (inset, the inorganic framework and the SDA). (B) TEM image of CDs@AlPO-5 composite showing CDs embedded in the inorganic matrix (inset, HRTEM image of a typical CD with a lattice spacing of 0.21 nm). (C) Excitation-emission two-dimensional plot of CDs@AlPO-5 composite. Emission intensity rises with the color changing from blue to green and to red. (D) Fluorescence microscopy images of CDs@AlPO-5 with ultraviolet (UV), blue, and green light excitation. (E to L) The SEM, TEM, HRTEM images, excitation-emission two-dimensional plots, and fluorescence microscopy images with UV, blue, and green light excitation of CDs@2D-AlPO and CDs@MgAPO-5, respectively.
under solvothermal/hydrothermal conditions. The CDs@AlPO-5 composite was solvothermally synthesized by using triethylamine (TEA) as the SDA in the reaction system of Al(OiPr)$_3$-H$_3$PO$_4$-TEA-HF-triethylene glycol (TEG) at 180°C for 3 days. The as-synthesized CDs@AlPO-5 crystals display hexagonal prism-like morphology (Fig. 2A), and their powder x-ray diffraction (PXRD) pattern reveals the characteristic diffraction peak of the AFI structure (fig. S1A). Liquid chromatography–high-resolution mass spectrometry (LC-HRMS) of the dissolved sample confirms the existence of TEA in the CDs@AlPO-5 composite (fig. S2). The transmission electron microscopy (TEM) image shows that uniform and monodispersed CDs are embedded in the AlPO-5 crystals with an average particle diameter of 3.7 nm (Fig. 2B and fig. S3A). Meanwhile, the CDs with a diameter of about 3.8 nm can also be observed in the synthetic mother liquid of CDs@AlPO-5 (fig. S4, A and B). The high-resolution TEM (HRTEM) image reveals a well-resolved lattice spacing of 0.21 nm, which is close to the (100) facet of graphite (27).

CDs@2D-AlPO composite was synthesized by using 4,7,10-trioxa-1,13-tridecanediamine (TTDDA) as the SDA in the solvothermal synthetic system of Al(OiPr)$_3$-H$_3$PO$_4$-TTDDA-TEG. Single-crystal XRD analysis reveals that the CDs@2D-AlPO has a layered [Al$_2$P$_3$O$_{12}$H]$_2$ structure, which is isostructural with the framework of aluminophosphate UT-5 synthesized by using cyclohexylammonium as the SDA (40). Prototinated TTDDA molecules are located in the layered structure (see Materials and Methods for more details on the synthesis and structure determination; the crystallographic tables, atomic coordinates, PXRD pattern, and structure of CDs@2D-AlPO are provided in tables S1 and S2 and figs. S1B and S5). As shown in Fig. 2E, the CDs@2D-AlPO crystals display plate-like morphology. TEM and HRTEM images show that the CDs with an average diameter of 3.5 nm are embedded in the CDs@2D-AlPO crystals (Fig. 2F and fig. S3B).

By using TTDDA as the SDA, CDs@MgAPO-5 was prepared in the hydrothermal reaction system of Al(OiPr)$_3$-MgHPO$_4$-3H$_2$O-H$_3$PO$_4$-TTDDA-H$_2$O at 180°C for 3 days. The obtained material has the AFI structure, as confirmed by PXRD study (fig. S1C), and displays polyhedral morphology (Fig. 2I). Well-dispersed CDs with an average particle diameter of 3.4 nm can be clearly observed in the zeolitic crystalline matrix (Fig. 2) and fig. S3C).

These CD-based TADF materials can be successfully prepared by in situ embedding luminescent CDs into zeolites and related open-framework materials in the presence of different organic templates and solvents. The simultaneous formation of CDs and zeolites under the solvothermal/hydrothermal conditions is crucial for the generation of CDs@zeolite composites. In contrast, in the conventional hydrothermal synthesis of AlPO-5 in the system of Al(OiPr)$_3$-H$_3$PO$_4$-TEA-HF-H$_2$O at 180°C, AlPO-5 was crystallized after 3 hours, but no CDs were observed in the mother liquid at the same time. Therefore, the resultant product shows no photoluminescent property.

**Excitation-dependent fluorescence of CDs@zeolite composites**

The as-synthesized CDs@AlPO-5, CDs@2D-AlPO, and CDs@MgAPO-5 composites show the characteristic excitation-dependent fluorescence behavior of CDs (Fig. 2, C, G, and K). The diluted mother liquids of CDs@zeolite also display similar excitation-dependent fluorescence to those of CDs@zeolite composites (fig. S4C). The observed emissions of CDs@zeolite composites can change from blue to green and to red with the prolonging excitation wavelengths (Fig. 2, D, H, and L). Strong deep blue emissions can be observed under a 370-nm excitation with the Commission Internationale de l’Eclairage (CIE) coordinates of (0.17, 0.13), (0.17, 0.14), and (0.17, 0.13) for CDs@AlPO-5, CDs@2D-AlPO,
Table 1. Photophysical characteristics of CDs@zeolite composites under ambient conditions excited at 370 nm. PL, photoluminescence.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>PL (nm)</th>
<th>CIE</th>
<th>QYS (%)</th>
<th>τ_{TADF} (ms)</th>
<th>ΔE_{ST} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDs@AlPO-5</td>
<td>430</td>
<td>0.17, 0.13</td>
<td>15.53</td>
<td>350</td>
<td>0.22</td>
</tr>
<tr>
<td>CDs@2D-AlPO</td>
<td>440</td>
<td>0.17, 0.14</td>
<td>52.14</td>
<td>197</td>
<td>0.23</td>
</tr>
<tr>
<td>CDs@MgAPO-5</td>
<td>425</td>
<td>0.17, 0.13</td>
<td>22.77</td>
<td>216</td>
<td>0.22</td>
</tr>
</tbody>
</table>

and CDs@MgAPO-5, respectively. The QYSs of these composite materials can be modulated by changing the host matrices and the reaction raw materials. The QYSs are changed from 15.53% for CDs@AlPO-5 to 22.77% for CDs@MgAPO-5 and up to 52.14% for CDs@2D-AlPO under the 370-nm excitation wavelength. The enhanced QYSs of CDs@2D-AlPO and CDs@MgAPO-5 over that of CDs@AlPO-5 may be attributed to the TTDDA SDA in the former two composites, which can produce and passivate the surface of CDs with enhanced photoluminescence QYSs according to the literature (41, 42). On the other hand, the QYSs of the CDs@2D-AlPO and CDs@MgAPO-5 composite materials are much higher than those of reported TTDDA-based CDs (12 to 13%). The improvements of QYSs are due to the efficient stabilization of CDs by the zeolite matrices.

**TADF property of CDs@zeolite composites**

Under UV excitation at 370 nm, the CDs@AlPO-5 emits deep blue light with emission centered at about 430 nm (deep blue line in Fig. 3A). The persistent luminescence can be seen by naked eyes at room temperature when the UV light is turned off. The emission band of the delayed fluorescence centers at 430 nm (blue line in Fig. 3A), which is consistent with that of the prompt fluorescence shown in the steady-state spectrum. The time-resolved decay spectra reveal the presence of both short- and long-lived species with lifetimes of 2.9 ns and 350 ns at room temperature, respectively (Fig. 3B). This demonstrates the coexistence of prompt fluorescence and delayed fluorescence for CDs@AlPO-5 composite. The temperature-dependent transient photoluminescence decay conducted from 100 to 350 K (as shown in Fig. 3C) shows that the ratio of the delayed component increases with the rising of temperature from 100 to 350 K, demonstrating that the delayed fluorescence phenomenon is influenced by the presence of thermal activation energy, which is characteristic for TADF-active materials (5, 19). The energy gap between the S1 and T1 excited state levels (ΔE_{ST}) has been further studied. The delayed spectrum measured at 77 K shows an emission band at 466 nm, which can be assigned as the emission of a triplet excited state (olive line in Fig. 3D). Compared with the steady-state photoluminescence spectrum at 77 K (deep blue line in Fig. 3D) with the emission band at 430 nm (the emission of a singlet excited state), an ΔE_{ST} value of 0.22 eV (S1, 2.88 eV; T1, 2.66 eV) can be obtained. The small energy gap (ΔE_{ST}) may make the RISC process from the T1 to S1 state possible when induced by room temperature thermal activation, thus facilitating the generation of TADF phenomenon.

As with CDs@AlPO-5, CDs@2D-AlPO and CDs@MgAPO-5 also exhibit the TADF behavior with long lifetimes of 197 and 216 ms, and their calculated ΔE_{ST} are 0.23 and 0.22 eV, respectively (figs. S6 and S7). Photophysical characteristics of these CDs@zeolite composites under ambient conditions excited at 370 nm are summarized in Table 1. Note that there is a negligible amount of adsorbed organic solvents/water in the CDs@zeolites that has an influence on the TADF properties (fig. S8 and table S3).

To understand the origin of TADF behavior, we studied the structure of CDs@AlPO-5 composite by x-ray photoelectron spectroscopy (XPS), UV-visible (UV-vis) absorption spectroscopy, and Fourier transform infrared (FTIR) spectroscopy (fig. S9). On the basis of the XPS analysis, the C–C–C/C bonds (284.6 eV), C–O/C–N bonds (286.3 eV), C=O/C=N bonds (287.6 eV), and pyridine-like (400.2 eV) and pyrrolic-like (402.2 eV) atoms can be identified (28). UV-vis absorption spectrum of CDs@AlPO-5 indicates the presence of n–π* transition of C=C bonds (263 nm) and n–π* transition of C=O/C=N bonds (350 nm) (25). The FTIR spectrum also shows the presence of C=O/C=N and C=O/C=N bonds (26). The C=O or C=N groups on CDs may facilitate the intrinsic triplet generation through intersystem crossing (43–46). As with CDs@AlPO-5, similar functional groups of CDs can also be found in CDs@2D-AlPO and CDs@MgAPO-5 composites (figs. S10 and S11).

Note that the CDs obtained in diluted mother liquid only show the short-lived fluorescence lifetime (5.1 ns) at room temperature (fig. S12). This suggests that the inorganic frameworks of zeolites play an essential role in stabilizing the long-lived triplet states. In the mother liquid, the excitations of isolated CDs are mainly deactivated through nonradiative routes at room temperature due to the active intramolecular vibrations and rotations. In contrast, the nanoconfined space in the rigid matrix of zeolites can effectively prevent the nonradiative relaxation by locking the emissive species and inhibiting their intramolecular motions. Note that the size of the CDs is much larger than the micropores in the zeolite structures; the CDs must be confined in the interrupted nanospaces. The interrupted framework of zeolites contains extensive dangling organic complexes and organic molecules. The enhanced lifetimes of the CDs@AlPO-5 composite was heated at 200°C under vacuum for 5 hours to sublime the organic SDAs, both the TADF lifetime and the delayed fluorescence can be clearly seen by naked eyes. As far as we know, the reported lifetimes of delayed fluorescence are mainly of several microseconds/milliseconds for the TADF materials of metal-organic complexes and organic molecules. The enhanced lifetimes of CDs@zeolite composites may be caused by the highly efficient stabilization of the zeolite framework and organic SDAs to effectively prevent the nonradiative relaxation and result in ultralong TADF behavior. Moreover, the CDs@zeolite TADF composite materials can work in air atmosphere, which is different from most traditional organic TADF materials in which the long-lived decay component would be greatly quenched at the air atmosphere because oxygen is a strong quencher of the triplet state emission.

The zeolite matrix is a good oxygen barrier that can effectively hinder the collisions between the functional groups and oxygen molecules.
long TADF can be clearly observed with naked eyes. Besides the switching off the excitation, only the flower represents ultralong delayed fluorescence blue, and the leaves and stem patterned with benzil dye molecules are green. When stem parts. Under a 365-nm UV excitation, the flower patterned with CDs@2D-AlPO is by the RISC process. P, phosphorescence. (vib) and rotations. Right: The terminal OH groups of the interrupted zeolite framework, quenched by nonradiative processes such as the active intramolecular vibrations (vib) and rotations. Right: The terminal OH groups of the interrupted zeolite framework, along with the occluded organic SDAs may form extensive H bonds with the surface functional groups of CDs to suppress the nonradiative relaxation of CDs derived from intramolecular vibrations and rotations and thus stabilize the triplet excited states. The small $\Delta E_T$ value of the CDs makes it possible for an efficient TADF emission facilitated by the RISC process. P, phosphorescence. (B) The security pattern of a rose is coded with the CDs@2D-AlPO as the flower part and the benzil dye molecule as the leaf and stem parts. Under a 365-nm UV excitation, the flower patterned with CDs@2D-AlPO is blue, and the leaves and stem patterned with benzil dye molecules are green. When switching off the excitation, only the flower represents ultralong delayed fluorescence that can be clearly observed by naked eyes, showing the time-resolved security features.

Moreover, the as-synthesized CDs@zeolite composites can keep their TADF property for more than half a year at air condition, showing their high stability (fig. S15 and table S5).

Dual-responsive security protection application

The advantages of CDs@zeolite TADF materials may open new perspectives for various delayed fluorescence–based applications. Here, we simply demonstrate a promising application of CDs@zeolite composites as a smart material for use in dual-mode security protection, in which traditional photoluminescence acts as one mode of security protection, whereas the visible TADF acts as the other mode with the persistent luminescence after the excitation for the lifetime-encoding feature. As shown in Fig. 4B, the security pattern of a rose is coded with two parts: the CDs@2D-AlPO as the flower part and the benzil dye molecule as the part of leaves and stems, which exhibit blue and green colors under a 365-nm UV excitation, respectively. When switching off the excitation, only the CDs@2D-AlPO–patterned flower part with ultralong TADF can be clearly observed with naked eyes. Besides the application as a smart material in dual-mode security protection, it is believed that the CDs@zeolite nanocomposites with long-lived TADF phenomenon can serve as ideal contrast agents for future high-sensitivity bioimaging for efficient avoidance of short-lived background fluorescence. TADF materials with long-lived excited states are also expected to be promising for solar cells because their long-lived excitons are enabled to extend diffusion distances for the efficient generation of free charges, which is a prerequisite for high-performance solar cells (9, 48).

CONCLUSIONS

We have successfully demonstrated a facile and general dots-in-zeolites strategy to prepare CD-based TADF materials with ultralong lifetimes by embedding CDs in nanoconfined spaces of zeolitic crystalline matrices. This approach is effective for the in situ incorporation of CDs derived from different organic species into various zeolitic host materials under hydrothermal/solvothermal conditions. The unique TADF property of these materials with ultralong-lived excited states at ambient conditions is benefited from the fact that zeolitic host matrices can effectively stabilize the triplet state by suppressing the nonradiative processes and hindering the oxygen quenching. The as-prepared CDs@zeolite composites display high QYs and ultralong lifetimes of up to 52.14% and 350 ms, respectively, which affirms their potential applications in security protection and future high-resolution bioimaging application. This method is generally applicable for other luminescent nanomaterials. The considerable flexibility of rational combination of photoluminescent nanodots and a wide range of suitable host matrices with well-confined nanospaces and electrical transport properties (for example, perovskite and TiO2) may facilitate the design of a variety of highly efficient TADF materials for advanced optoelectronic device applications (for example, solar cells and LED). This discovery of a new class of CD-based TADF materials with ultralong lifetimes and high efficiency is developed as a proof of concept, which we believe will promote both fundamental understanding and future practical applications of TADF materials.

MATERIALS AND METHODS

Materials

All reagents were used without purification. Aluminum isopropoxide (≥98% purity) and TTDDA (97% purity) were obtained from Sigma-Aldrich. $\text{H}_3\text{PO}_4$ [85 weight % (wt %) in water] and hydrogen fluoride (HF; 40 wt % in water) were supplied by the Beijing Chemical Reagent Factory. TEG and MgHPO4·3H2O were obtained from Aladdin Chemical Reagent Co. High-purity water was obtained from Milli-Q purification system. TEA (99% purity) was obtained from Tianjin Fuyu Fine Chemical Co. Ltd.

Synthesis of CDs@zeolites

CDs@AlPO-5 was synthesized using TEA as the SDA under solvothermal conditions. In a typical synthesis of CDs@AlPO-5, aluminum isopro- propoxide was dispersed in a mixture of TEG and $\text{H}_3\text{PO}_4$. Then, TEA and HF were dispersed into the mixture with stirring. A homogeneous gel was formed with an overall molar composition of 1.0 $\text{Al}_{2}\text{O}_3$:1.3 $\text{P}_2\text{O}_5$:1.6 TEA:1.3 HF:17 TEG. After crystallizing at 180°C for 3 days, the crystalline product was separated, thoroughly washed with distilled water, and dried at room temperature overnight.

CDs@MgAPO-5 and CDs@2D-AlPO were synthesized by using TTDDA as the SDA. In a typical synthesis of CDs@MgAPO-5, aluminum isopro- propoxide was dispersed in a mixture of water and $\text{H}_3\text{PO}_4$. [Image 55x419 to 272x700]
Then, MgHPO₄·3H₂O and TTDDA were dispersed into the mixture with stirring. A homogeneous gel was formed with an overall molar composition of 1.0 Al₂O₃·1.9 P₂O₅·2.0 TTDDA·18 TEG·3.7 H₂O. After crystallizing at 180°C for 3 days, the crystalline product was separated by washing with distilled water and drying at room temperature overnight. As for the synthesis of CDs@2D-AIPO, aluminum isopropoxide was dispersed in a mixture of TEG and H₃PO₄. Then, TTDDA was dispersed into the mixture with stirring. A homogeneous gel was formed with an overall molar composition of 1.0 Al₂O₃·1.9 P₂O₅·2.0 TTDDA·18 TEG·3.7 H₂O. After crystallizing at 180°C for 3 days, the plate-like crystalline product was obtained by washing with distilled water and drying at room temperature overnight.

The percentages of CDs incorporated in the CDs@zeolite composites were evaluated according to the CHN analysis by comparing the CDs@zeolites with the pure zeolite analogs synthesized with the same SDAs. The percentages of CDs calculated on the basis of C content in CDs@MgAPO-5 and CDs@2D-AIPO were 0.55 and 0.64 wt %, respectively. However, the percentage of CDs in CDs@MgAPO-5 was difficult to provide because no pure MgAPO-5 could be synthesized by using the same SDA.

Apparatus and measurements

PXRD data were collected on a Rigaku Ultima IV diffractometer with Cu Kα radiation (λ = 1.5418 Å). The TEM and HRTEM images were taken on an FEI Tecnai G2 S-Twin F20 TEM and FEI Titan G2 60–300 scanning TEM. The infrared absorption spectra were recorded on a Bruker FTIR IFS-66/V/S spectrometer in the range of 400 to 4000 cm⁻¹ with KBr pellets. A baseline correction was applied after measurement. UV-vis adsorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer. The XPS measurements were performed using a Thermo ESCALAB 250 spectrometer with monochromatized Al Kα excitation. LC-HRMS was performed on a high-performance liquid chromatography (Agilent 1290) and HRMS (microTOF-Q II, Bruker Daltonics). Thermogravimetric (TG) analysis was performed on a TA Q500 analyzer in air from room temperature to 800°C at 5°C/min. CHN analysis was conducted on a PerkinElmer 2400 elemental analyzer.

Photoluminescence measurements

Excitation-emission two-dimensional plots, steady-state spectra, and delayed photoluminescence spectra were obtained by using a HORIBA Scientific FluoroMax-4 spectrofluorometer. The fluorescence lifetime spectra were performed with a HORIBA Scientific FluoroMax-4 by using FluorHub-B fluorescence lifetime system equipped with a photomultiplier tube detector. A nanoLED and a microsecond flash xenon arc lamp were used as the excitation sources. Ludox was used to calculate instrument response factor (IRF). The data were analyzed using DAS6 software using a multiexponential model for lifetime. The average lifetimes (τₑ) can be calculated with τₑ = ΣAᵢτᵢ²/ΣAᵢτᵢ, where Aᵢ is the preexponential for lifetime τᵢ (Aᵢ and τᵢ of the CDs@zeolites and diluted mother liquid are shown in table S6). The fluorescence images were taken using an Olympus BX51 at UV, blue, and green light excitations through bandpass filters of 450-, 550-, and 580-nm wavelengths. Temperature-dependent transient photoluminescence decay was measured using an Edinburgh FLS920 fluorescence spectrophotometer equipped with a microsecond flashlamp. The fluorescence QY was measured on a Bruker SMART APEX II CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at a temperature of 23° ± 2°C. Cell refinement and data reduction were accomplished with the SAINT processing program. The structure was solved in the P2₁/c space group by direct methods and refined by full-matrix least-squares technique with the SHELXTL crystallographic software package. The heaviest atoms of Al, P, and O could be unequivocally located, and the C and N atoms were subsequently located in the difference Fourier maps.

Single-crystal XRD

Suitable single crystal of CDs@2D-AIPO with dimensions of 0.23 mm × 0.21 mm × 0.20 mm was selected for single-crystal XRD analysis. The intensity data were collected on a Bruker SMART APEX II CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at a temperature of 23° ± 2°C. Cell refinement and data reduction were accomplished with the SAINT processing program. The structure was solved in the P2₁/c space group by direct methods and refined by full-matrix least-squares technique with the SHELXTL crystallographic software package. The heaviest atoms of Al, P, and O could be unequivocally located, and the C and N atoms were subsequently located in the difference Fourier maps.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/5/e1603171/DC1

fig. S1. PXRD patterns.

fig. S2. LC-HRMS of dissolved CDs@AlPO-5 composite.

fig. S3. The particle diameter distributions of CDs in CDs@zeolite composites.

fig. S4. TEM analysis and photoluminescence property of CDs in the diluted mother liquid of CDs@AlPO-5.

fig. S5. Structure of 2D-AIPO synthesized by using TTDDA as SDA.

fig. S6. TADF properties of CDs@2D-AIPO composite.

fig. S7. TADF properties of CDs@MgAPO-5 composite.

fig. S8. TADF properties of CDs@zeolite composites after vacuum drying for 12 hours at room temperature.

fig. S9. The compositional analysis of the organic species in CDs@AlPO-5 composite.

fig. S10. The compositional analysis of the organic species in CDs@2D-AIPO composite.

fig. S11. The compositional analysis of the organic species in CDs@MgAPO-5 composite.

fig. S12. The time-resolved decay spectrum of the CDs in the diluted mother liquid of CDs@AlPO-5 at room temperature.

fig. S13. PXRD and TG characterizations of CDs@AlPO-5 composites vacuum-calcined at different temperatures.

fig. S14. TADF properties of CDs@zeolite composites after vacuum drying for 12 hours at room temperature.

fig. S15. TADF properties of CDs@zeolite composites kept under ambient conditions for more than half a year.

table S1. Crystal data and structure refinement for CDs@2D-AlPO.

table S2. Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (Å² × 10⁴) for CDs@2D-AIPO.

table S3. The photoluminescence emission bands and lifetimes of CDs@zeolite composites after vacuum drying at room temperature.

table S4. The photoluminescence emission bands and lifetimes of CDs@zeolite composites after vacuum calcination at different temperatures.

table S5. The photoluminescence emission bands and lifetimes of CDs@zeolite composites before and after half a year under ambient conditions.

table S6. The multietepal (A) and preexponential for lifetime (A) of the CDs@zeolite composites and the diluted mother liquid.

data file S1. CIF file for CDs@2D-AIPO.

data file S2. CheckCIF file for CDs@2D-AIPO.

REFERENCES AND NOTES


Acknowledgments: We thank Y. Wang (Jilin University), Q. Zhang (Zhejiang University), Y. Tao (Nanjing Tech University), and R. Chen (Nanjing University of Posts and Telecommunications) for helpful discussions. Funding: This work was supported by the National Key Research and Development Program of China (grant no. 2016YFB0701100), the National Natural Science Foundation of China (grant nos. 21320102001, 21621001, 21671075, and 91122029), and the “111” Project of the Ministry of Education of China.
Author contributions: J.Y. supervised and coordinated all aspects of the project. J. Li also coordinated this work. J. Liu carried out synthesis and characterization, interpreted the data, and wrote the paper. N.W. performed the TEM and HRTEM measurements. Y. Yu conducted the dual-mode security protection experiments. Y. Yan solved crystal structures and performed data fitting. H.Z. did part of the experiments and related analyses. J.Y. and J. Li revised the manuscript. All authors discussed and commented on the manuscript. Competing interests: The authors declare that they have no competing interests. Data and materials availability: CCDC 1517735 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data_request/cif). All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 14 December 2016
Accepted 22 March 2017
Published 26 May 2017
10.1126/sciadv.1603171

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Sci Adv 3 (5), e1603171.
DOI: 10.1126/sciadv.1603171