Graphitic Dots Combining Photophysical Characteristics of Organic Molecular Fluorophores and Inorganic Quantum Dots

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ABSTRACT: Thanks to their photophysical properties, both organic molecular fluorophores (MFs) and inorganic quantum dots (QDs) are extensively used for bioimaging applications. However, limitations such as photobleaching for the former or blinking, size, and toxicity for the latter still constitute a challenge for numerous applications. We report here that embedding MFs in graphitic carbon dots (GDs) results in fluorophores which entirely tackle this challenge. Characterized by ultranarrow, bright, and excitation-independent emission devoid of blinking and photobleaching, these hybrid-featured nanoparticles also demonstrate their unique photophysical performances at the single-nanoparticle scale, making them appealing candidates for bioimaging applications.

KEYWORDS: graphitic carbon dot, fluorophore, blinking, photobleaching, photophysics, microscopy

INTRODUCTION

The quest toward graphitic carbon dots (GDs) with photophysical properties outclassing inorganic quantum dots (QDs) remains unfulfilled. Despite their high colloidal stability, biocompatibility, and cost-effectiveness, GDs are still hampered by unattractive photophysical features such as broad and excitation-dependent photoluminescence (PL) bands, multiple decay rates indicating underlying complex photophysical mechanisms, low quantum yield, and fluorescence blinking.1−4 The latter phenomenon also occurs with inorganic QDs.5−7 By contrast, the PL of molecular fluorophores (MFs) is generally characterized by a high quantum yield and a single-decay emissive process, even though this PL is sensitive to photobleaching and to change in the environment (pH, solvent, temperature, and probe concentration). Combining the structures of both a GD and a MF would conceptually lead to nanoparticles with powerful hybrid features. Such GDs could eventually compete with inorganic QDs in displays,8−12 bioimaging,4,13−17 and fluorescence nanothermometry,18−23 applications, yet using nontoxic and abundant organic materials with favorable life cycle assessments. Here, we present a novel design of nanoparticles where MFs of a single type are embedded into GDs (MFGDs), thus exhibiting desirable features of both components. The carbon matrix acts as a shield isolating the MFs from the environment, thus ensuring strong and constant monochromatic emission. On the other hand, the outer polymeric hairy layer provides remarkable dispersibility and colloidal stability to the whole nanoparticle, without screening the core from excitation photons. Such a unique set of properties was achieved by patterning the architecture of the GDs after a self-assembled block copolymer containing a graphitizing segment24 and by carefully controlling the conditions under which the graphitizing segment is converted into a GD (Figure 1). Resulting MFGDs exhibit a monochromatic emission at 547 nm (fwhm <30 nm) with a quantum yield of ~70%, a single fluorescence decay of ~4 ns, and a complete absence of blinking at the single-nanoparticle scale. Our facile approach provides a robust general route to prepare MFGDs, thus stimulating additional developments in their understanding and application in the field of biological imaging.

RESULTS AND DISCUSSION

Our approach relies on the graphitization of self-assembled polymeric micelles. First, the block copolymer precursor P(TBA-b-AGA) is assembled in polymeric micelles (Figure 2A steps III−IV and Figure 2B) where the glucosamine-containing P(AGA) forms the core and the P(TBA) forms the outer hairy layer. The size of the micelles decreases from 230 to 100 nm (Figure S9) when the DMSO:1-heptanol volume ratio changes from 5:5 to 2:8, as progressive desolvation of the

Received: February 9, 2021
Published: May 11, 2021
core of the micelle occurs with greater amounts of 1-heptanol. Then, these polymeric micelles are graphitized. At 180 °C, the P(AGA) block is transformed into sp² carbon domains (see below). Concomitantly, the P(TBA) is converted into poly(acrylic acid), P(AA) as revealed by Fourier-transform infrared spectroscopy (FTIR, Figure S7D and Table S1), thermal gravimetric analysis (TGA, Figure S10, P(TBA) is thermally cleaved into P(AA)), and X-ray photoelectron spectroscopy (XPS) (Figure 3D). The resulting particles exhibit an isoelectric point around pH = 5 which is characteristic of carboxylic acids, as measured by ζ potential (Figure S12).

Resulting MFGDs (Figures 1 and 2A, step IV) consist of a graphitic core decorated with a hairy P(AA) layer which imparts colloidal stability in polar solvents such as DMF, water, DMSO, THF, and alcohols (Figure S14) and which can be used to conjugate biomarkers. A solution of MFGDs has been stored for 2 years without any noticeable aggregation or loss of photophysical properties. Analysis by TGA (Figure S13) reveals a mass loss of ~50% below 450 °C, which indicates that the polymeric hairy layer accounts for 50% of the MFGD mass. Applying our graphitization procedure to homopolymers results in different materials (Figure S26). Indeed, P(TBA) gives a yellow polymer that weakly emits, while P(AGA) results in a brown powder with low emission (Figure S26) and poor dispersibility. Graphitization of P(TBA-b-AGA) in DMSO (freely dissolved precursor i.e. not self-assembled) gives similar results to P(AGA). These control experiments demonstrate that MFGDs fluorescence arises from the P(AGA) block graphitization, but that self-assembly is necessary to ensure MFGDs properties. The control of the temperature at 180 °C is also crucial to obtain MFGDs (Figure S11). Varying the block copolymer concentration from 3 to 12 g·L⁻¹ has no noticeable effect on the MFGDs emissive properties. These observations can be explained considering that each polymeric reverse micelle is equivalent to a nanoreactor containing highly concentrated glucosamine readily transformed into a graphitic nanoparticle upon heating. Therefore, MFGDs are only obtained when the glucosamine is confined in a nanoreactor and shielded from interparticle side reactions. Furthermore, analysis by size exclusion chromatography (Figure S18) reveals that there is no dissolved MF outside the GDs: MF and GDs belong to a single entity.
The MFGDs size distribution measured through transmission electron microscopy (TEM, Figures S15 and S16) does not significantly differ from size distributions commonly reported for GDs (d = 2.2 nm, σ = 0.6 nm), suggesting that the emission narrowness and excitation independence is not originating from a single-size effect. High-resolution TEM (HR-TEM, Figure 3A and Figure S17) images show lattice fringes with a period of 0.21 nm, corresponding to the (100) planes of graphitic carbon. Powder X-ray diffraction (XRD) shows two broad peaks centered at 2θ = 19.2° and 2θ = 38.0° (Figure 3B), assigned respectively to the (002) and (101) planes of nanographite (JCPDS no. 75-1621). Raman spectrum (Figure 3C) shows two peaks at 1335 and 1580 cm⁻¹, corresponding respectively to the D-band and G-band of graphitic carbon, with an intensity ratio of 1.05, an expected value considering the small size of the GD (most of the atoms are close to the surface). The MFGDs were also analyzed by XPS. Importantly, both the graphitic core and the P(AA) chains are indistinctly surveyed. The C 1s peak (Figure 3D) was deconvoluted into four peaks at 284.7, 286.0, 287.2, and 288.5 eV, corresponding respectively to carbon–carbon bonds (C–C, C=C), carbon–heteroatoms bonds (C–O, C=N), carbonyls (C=O), and carboxylic acids (COOH) (O 1s peak also presented on Figure S19). The presence of ~4% nitrogen (Figure S20) in MFGDs originates from the nitrogen atom present in glucosamine. The high-resolution XPS analysis of the N 1s peak (Figure S21) highlights the presence of pyridinic, pyrrolic, amide, and graphitic N, respectively, at 397.2, 399.7 (pyrrolic + amide), and 401.0 eV. As both pyridinic and graphitic N correspond to N-doped graphitic structures, the MFGDs are then slightly N-doped (0.8–0.9% based on XPS integration). The determination of a low donor density value N_d for the MFGDs through the Mott–Schottky plot further confirms this slight N-doping (Figure S22). Our structural and morphological characterizations indicate that MFGDs are slightly N-doped graphitic carbon nanoparticles decorated with a P(AA) hairy layer. Notably, our synthetic route does not require any high-pressure reactor and is easily scalable. Using conventional laboratory equipment, batches of ~2 g of MFGDs were achieved.

An emission map of the MFGDs in DMF, acquired by exciting them between 300 and 700 nm (Figure 4H), reveals two features. The first one is a dominant emission centered at 547 nm, and present at all excitation wavelengths. The second one is a weak emission centered at 485 nm (Figure S25A inset). This weak emission is red-shifting with increasing excitation wavelength from 300 to 450 nm (Figure 4A inset). Although the excitation-dependent PL is a characteristic of GDs, the quasi-monochromatic 547 nm emission is unusual for such nanomaterials (fwhm of 26–27 nm in DMF). Using water as the solvent instead, the PL spectrum is similar (fwhm of 29–34 nm) but with the main emission at 530 nm (Figure 4B and Figure S25C,D). Dispersed in a polymer matrix, the PL emission is still dominated by a monochromatic emission at 535 nm (Figure S25C). Dried MFGDs appear as a dark crimson powder (Figure S23) spontaneously (re)dispersible in polar solvents (including water) thanks to their P(AA) hairy layer. The attenuation coefficient of the resulting solution was found to be $\varepsilon = 5.21 \text{ L·g}^{-1} \cdot \text{cm}^{-1}$ in DMF, which corresponds to $\varepsilon = 3.15 \times 10^4 \text{ L·mol}^{-1} \cdot \text{cm}^{-1}$ (see Figure S30). The strong fluorescence of MFGDs dilute solutions makes their color change depending on their illumination (Figure 4E). Namely, back-illumination makes them appear crimson, in accordance with their absorption spectrum (Figure 4G), whereas front-illumination makes them appear green/yellow, as expected from the mixing of weak blue and intense yellow emissions. The hardly noticeable change in the emission color with varying excitation wavelength is due to the rise and fall of the weak emission centered at 485 nm and is not originating from
any kind of spectral shift (Figure S28). Remarkably, concentrated MFGDs solutions appear brick-red to the naked eye and turn greener and greener with increasing dilution (Figure 4F). Due to the high particle concentration, the intense yellow emission is reabsorbed by neighboring particles, allowing only the red color to be transmitted out of the solution (Figure 4F).

The excitation spectrum of diluted MFGDs was measured by probing the emission at 580 nm (Figure 4G), revealing a dominant sharp excitation band centered at 540 nm with a shoulder at 503 nm. These excitation bands correspond perfectly to the observed absorption bands and confirms that the emission at 547 nm stems from the same excited state populated at these absorption wavelengths. Furthermore, when the emission map is sliced along the excitation wavelength axis (Figure 4H), the same excitation spectrum is produced for all emission wavelengths, indicating that there is a single emissive species in solution. Another feature of the excitation spectrum is a very weak excitation band centered at 400 nm, which explains the low emission noted at 547 nm with near UV excitation. The strong UV absorption that tails off through the visible region, commonly attributed to carbon absorption in GDs, is absent from the excitation spectrum, suggesting that this absorption originates from another species or state which is unrelated to the 547 nm emission. The excitation spectrum shows a structure that is the mirror image of the emission spectrum, as commonly seen for MFs. The shoulders in the excitation spectrum and emission spectrum, located at 503 and 597 nm respectively, are tentatively assigned to vibronic bands issued respectively from the 0→1 excitation and the 0→1 relaxation. The difference in energy between maxima and their corresponding shoulders corresponds to vibrational frequencies of 1362 and 1531 cm⁻¹ (respectively on the excitation and emission spectra), suggesting that a π-conjugated fluorophore is at stake. In order to confirm that the difference between the absorption and excitation spectra is not due to light scattering, the absorption spectrum was taken in a diffuse reflectance mode (Figure S29). It was found to be identical to the one acquired in transmission, indicating that the UV absorption feature which tails off through the visible region to the NIR is in fact a true absorption and is neither associated with an emissive state nor with light-scattering. These conclusions suggest that MFGDs consist of a graphite matrix which absorbs a continuum of light and which encapsulates a conjugated fluorophore. In order to assess whether the intense emission arises from the recombination caused by trapped surface states, the emission of the MFGDs was measured at various concentrations (Figures S27B,C). This investigation was performed in a front-facing configuration, as a strong secondary inner-filter effect altered the shape of the PL emission when measured in a classical configuration (Figures S31 and S32). As the PL is not affected by concentration, the MFGDs are not prone to interact with each other through surface interactions.

Given that steady-state measurements suggest that the structure of a MFGD consists of fluorophores embedded in a carbon matrix, one expects to observe a certain degree of competitive absorption between the emissive fluorophore and the nonemissive matrix. For this reason, excitation at different wavelengths could favor either the excitation of the fluorophore or the absorption of the graphic matrix, respectively resulting in excitation-dependent quantum yield (Figure 4G). With an excitation wavelength of 500 nm where a large proportion of the emissive species is excited, the average quantum yield (QY) reaches ∼71% (Figure S35), whereas it decreases to ∼29% and ∼10% with excitations at 485 and 470 nm respectively (Figures S33 and S34). This variable value of QY lends credence to the proposed structure of the MFGDs, as variations of this magnitude can only be explained by the competitive absorption between species. It is important to note that the fluorophore itself is not expected to have a highly variable QY and that the values reported here are apparent QY, which can be described as the ratio of the number of photons emitted by the fluorophore over the number of photons absorbed by the carbon matrix and the fluorophores. The very high QY of the fluorophore (which is at least 71%) can be explained by the fact that the embedded fluorophore is kept in an isolated environment where it cannot interact with solvent molecules or oxygen (no attempt to degas was made), thus limiting nonradiative relaxation pathways.

Time-resolved emission spectroscopy (TRES) was performed on a diluted MFGDs solution to show that the entire emission relaxes with the same kinetics, thus confirming a single emissive state is at stake. This was done by stacking time-correlated single-photon counting (TCSPC) decay traces (λ_{excitation} = 477 nm @ 5 MHz) acquired at different emission wavelengths over the same integration time (Figure 5A). The decay was found to have a lifetime ranging from 3.6 to 4.3 ns (3.9 ns in average) over the entire spectrum (Figures S36 and S37 and Tables S2 and S3). The quasi-absence of variation in the relaxation kinetics (Figure 5B) suggests that the earlier assignment of the shoulder at 597 nm as a vibronic progression is accurate. The decay rate is also not affected by the concentration of the sample (Tables S2–S3), further corroborating that the fluorophores are not at the surface.

Femtosecond transient absorption spectroscopy (fs-TAS) was performed through three separate experiments to search for any ultrafast relaxation pathway. Namely, exciting the sample at 530, 480, and 397 nm probed the emission kinetics. When excited at 530 nm (Figure 5C,D) and 480 nm (Figure S40), the fs-TAS is dominated by two signals. The first and prevailing one, with a maximum at 542 and 594 nm, is assigned to a superposition of ground-state bleaching and stimulated emission of the MFGDs. The second feature centered at 415 nm corresponds to the absorption of the emissive excited state based on its spectral similarities with the weak excitation band observed on the steady-state excitation spectrum (Figure 4G). When excited at 480 nm, similar kinetic behavior is observed (Figures S40A–S40B). The entire fs-TAS surface is relaxing at the same rate, suggesting that the excited-state relaxation is largely dominated by a single process. Deconvolution of the spectra recorded with excitation at 480 and 530 nm required the application of three exponential components (Table S6), however deconvolution also shows that the recovery of the ground state is dominated by a single kinetic process. The other components, which are fast processes with lifetimes of ∼1.5 ps and ∼50 ps (Figures S42A,B, S39B, and S40B), are of very low intensity and are tentatively assigned to the relaxation of an upper excited state and to the dissipation of energy through interaction with the solvent or the carbon matrix surrounding the fluorophore. These fast processes could also be attributed to the relaxation of the carbon matrix itself as it is inevitably excited by the pump laser. The most intense kinetic component has a lifetime between 3.64 and 3.82 ns and has a decay-associated spectrum.
Transient transmittance (Figures S41B and S42C). At the ns-time scale, once the above-mentioned contribution has ceased, the signal is clearly dominated by a broad excited-state absorption covering the entire visible region and resulting in an overall negative signal at two distinct features appear (Figures S41A). First, a positive shoulder at 594 nm, corresponding to the stimulated emission component for nonradiative decay via vibrational cooling further suggests that there is actually no communication between the fluorophore and the matrix or the environment. This conclusion is also supported by the weak yellow emission observed when exciting in the UV (Figure 4A,B insets).

Forster resonant transfer occurs between adjacent MFs, then the rapid energy exchange results in energy hopping and an immediate loss of polarization, leading to a vibronic thermalization, based on assignments of the DAS for this 2.0–2.6 ns lifetime component (Figure S43C), the 1.9–2.0 ns lifetime from TCSPC is clearly associated with the fluorescence emission of the embedded fluorophore. A similar lifetime of 2.7–2.8 ns is observed when the emission is probed at 547 nm and is thus assumed to originate from the same excited state. Furthermore, the increase in fluorescence intensity percentage ($f$) from $\lambda_{\text{emission}} = 485$ to 547 nm (Tables S4 and S5) corroborates that the embedded fluorophore is at state. Indeed, although the fluorophore mostly emits around 547 nm, there is still a small contribution from the base of the band that overlaps the carbon matrix emission (Figure 4A inset). The other major contribution to the emission found through TCSPC has a lifetime of 4.8–4.7 ns at 485 nm and 5.3 ns at 547 nm (Tables S4 and S5). These close lifetime values also suggest that a single excited state is involved. These lifetimes are thus assigned to the carbon matrix emission based on similarities with reported values in GDs literature$^{26,27}$ and decreasing the fluorescence intensity percentage from 485 to 547 nm. To summarize this section, the drastic change in the fs-TAS spectrum when exciting at 397 nm is assigned to the fact that the carbon matrix is more excited than the MF. The broad excited-state absorption signals, that relaxes with two kinetic rate constants yielding lifetimes in the ranges 4.0–4.6 ps and 36–43 ps, are respectively assigned to an excited-state absorption phenomenon and to a vibronic thermalization, based on assignments from GD-related literature (see below Table S6). The fact that the fs-TAS shows only a weak signal associated with the emissive state when excited at 397 nm and only a very small component for nonradiative decay via vibrational cooling further suggests that there is actually no communication between the fluorophore and the matrix or the environment. This conclusion is also supported by the weak yellow emission observed when exciting in the UV (Figure 4A,B insets).

The above results demonstrate that we have formed GDs decorated by a polymeric layer (PAA) and containing MFs that do not exchange energy with the carbon matrix or the environment when excited at $\lambda_{\text{exc}} = 530$ nm. However, if several MF molecules were embedded within the GD, we could expect to observe Forster resonant transfer between them, considering the small size of single GD (core size = 2.2 nm) that would lead to energy hopping. To probe for the presence of such transfer mechanism, fluorescence anisotropy measurements were performed. A MFGD particle has a hydrodynamic radius which is at least 3 nm (taking into account the hairy polymeric layer). Thus, the calculated rotational lifetime must be at least 22 ns (see Figure S48). As the number-average decay time equals 3.2 ns, an isolated fluorophore can be considered as immobile (no tumbling) during most of its emission process ($r = r_0$ where $r$ and $r_0$ are, respectively, the fluorescence anisotropy at time $t$ and $t_0$). If Forster resonant transfer occurs between adjacent MFs, then the rapid energy exchange results in energy hopping and an immediate loss of polarization, leading to $r = 0$. Time-resolved anisotropy measurements (Figure S47 and Table S7)
demonstrate that there is no change in the fluorescence decays when working with various polarizations, indicating that either \( r = 0 \) (energy transfer leads to isotropic emission) or \( r = r_0 \) (emission occurs before tumbling occurs). Remarkably, steady-state fluorescence anisotropy measurement demonstrates that \( r = 0.042 \pm 0.009 \). This nonzero value rules out the presence of Forster resonant energy transfer between neighboring MFs. Thus, this experiment reveals that each GD particle contains a single MF.

Single-nanoparticle imaging (SNI) and temporal fluorescence spectroscopy (TFS) are suitable microscopy tools for probing the emissive behavior of an isolated nanoparticle in a specific environment. MFGDs dispersed in an aqueous acrylamide gel (Figure S44) had a Brownian motion slow enough to prevent frame-to-frame drift over the whole imaging time in SNI. MFGDs appear as bright dots on a dark background, with apparent submicrometer diameters varying with their respective position regarding the focal plan (Figure S45). Using the confocal mode, in-plane MFGDs appear as neat round-shaped dots of identical apparent diameters (Figure 6A). As TEM images reveal that the MFGDs are not aggregated, each dot corresponds to an isolated MFGD. Remarkably, isolated MFGDs emission shows no fluctuation in intensity, blinking or photobleaching under continuous laser excitation at 488 nm (Figure 6B). The MFGDs photostability in nondegassed water was also assessed by continuous monochromatic excitation at high irradiance \( 160 \text{ W}\cdot\text{m}^{-2} \) at 460 nm and emission intensity monitoring at 532 nm (Figure 6C). The PL intensity remains identical over the 6 h irradiation, thus demonstrating that a negligible photobleaching phenomenon occurs within the MFGDs. The absence of blinking in addition to insignificant photobleaching supports the model of embedded fluorophores inside a graphitic carbon matrix: The absence of blinking is a typical behavior of a molecular fluorophore, whereas the outstanding photostability strongly corroborates that the fluorophores are effectively sheltered from the medium.

### Conclusion

MFGDs, that is, nanoparticles combining the emissive properties of a single MF and the stability of a GD, have been synthesized by graphitizing polymeric reverse micelles through a facile setup. These hybrid properties originate from a single type of conjugated molecular fluorophore embedded in the nanoparticle graphitic carbon core. Fluorophores isolation ensures their photostability and favors a clean-cut photophysical mechanism ruled by a single emissive state and a single fluorescence lifetime. As a result, MFGDs are exempt of photobleaching and blinking, which are two significant hurdles in the application of MF and GD for bioimaging applications.

### Experimental Section

**Materials**

All the chemicals involved in the syntheses and media preparation were commercially available and used as received unless otherwise stated. In particular, solvents were used without drying either for the graphitization step (dimethyl sulfoxide, 1-heptanol) or for photo-physical characterizations (dimethylformamide). Nanopure water \( (\rho = 18.2 \text{ M} \cdot \text{cm}) \) was used for synthesis purpose and pH buffer solutions preparation (Figures S12–S42) and as a dispersion media for the MFGDs. Monomers, RAFT agent, and 2,2’-azobis (2-methylpropionitrile) thermal free-radical initiator (AIBN) were stored in a refrigerator when not in use. More exactly, the TBA monomer was stored as received whereas di-tert-butyl-p-cresol (BHT) was added to the freshly synthesized PPFA monomer (0.1 w%) prior to any prolonged storage. Monomers were distillated over additional BHT (1 w%) before polymerization, whereas RAFT agent and AIBN were recrystallized, respectively, from boiling hexane and methanol, then dried under vacuum at room temperature. For the preparation of MFGDs-containing gel 4,4’-azobis(4-cyanovaleric acid), thermal free-radical initiator (ACVA) was recrystallized from boiling methanol.

**Synthesis of 2-[(Butylsulfanyl)carbonothioyl]sulfanyl) Propanoic Acid (RAFT Agent)**

The RAFT agent was synthesized as reported by Hawkett et al. \(^{28} \) with minor modifications. To a biphasic mixture of water (60 mL) and butanethiol (43 mL, 401 mmol) were added NaOH (16 g, 400 mmol, dissolved in 16 mL H\(_2\)O) then acetone (20 mL). After full homogenization and cooling down, carbon disulfide (27 mL, 450 mmol) was slowly added with a syringe upon vigorous stirring. The resulting orange solution was stirred for an additional 30 min following which the medium was cooled in an ice bath. Using a syringe, 2-bromopropionic acid (37 mL, 410 mmol) was added dropwise, and additional NaOH (16.4 g, 410 mmol, dissolved in 16.4 mL H\(_2\)O) was subsequently poured slowly, still for the sake of mitigating the reaction exotherm. Upon complete cool down, water (60 mL) was added, and the whole reaction was stirred overnight at room temperature. Additional water (100 mL) was poured in, and the reaction medium was cooled again using an ice bath, following which HCl (\( \sim 40 \text{ mL}, \sim 480 \text{ mmol}, \) mixed with 40 mL H\(_2\)O) was added at a rate slow enough so that the exotherm did not exceed the room temperature. Upon stirring, still at low temperature, the separating yellow phase solidified and was filtered on a büchner funnel, then thoroughly washed with water while being triturated at the same time. The yellow solid was roughly air-dried on the suction filtration setup and then vacuum-dried overnight at room temperature. Recrystallization from hexane gave bright yellow fine crystals that were ground into powder and then stored in fridge in a tightly sealed container \( (82.0 \text{ g}, \eta = 86\%) \). \(^1\text{H} \) NMR (CDCl\(_3\)) \( \delta \) (ppm): 9.4 (br, CO\(_2\)H), 4.87 (q, \( J = 7.4 \text{ Hz})\), 3.37 (t, \( J = 7.4 \text{ Hz})\), 2H, CH\(_2\)CH\(_2\)S), 1.69 (quint, \( J = 7.4 \text{ Hz})\), 2H, CH\(_2\)CH\(_2\)S), 1.63 (d, \( J = 7.4 \text{ Hz})\), 3H, SCH\(_2\)H), 1.44 ( sext, \( J = 7.4 \text{ Hz})\), 2H, CH\(_2\)CH\(_2\)), 0.94 (t, \( J = 7.3 \text{ Hz})\), 3H, CH\(_2\)CH\(_3\)).
Synthesis of PFPA Monomer

The PFPA monomer was synthesized according to the procedure reported by Théato et al.\textsuperscript{29} with minor modifications. Pentafluorophenol (32.4 g, 176 mmol) and then 2,6-lutidine (21 mL, 180 mmol) were dissolved in methylene chloride (200 mL). After cooling the resulting clear solution using an ice bath, acryloyl chloride (14 mmol) were dissolved in methylene chloride (200 mL). After cooling the solution was washed with brine (2 × 70 mL) and dried over MgSO\(_4\). Remaining methylene chloride was removed under vacuum, at room temperature, using a rotary evaporator. The resulting clear pinkish liquid was subsequently purified through high-vacuum distillation.

The first fractions were discarded, and the PFPA was finally recovered as a clear and uncolored liquid (31.4 g, \(\eta = 75\%\)). \(^1^H\) NMR (CDCl\(_3\)) \(\delta\) (ppm): 1.64 (dd, \(J = 1.1\) and 17.2 Hz, 1H, \(H_{\text{geminal-trans}}\)), 6.37 (dd, \(J = 10.5\) and 17.2 Hz, 1H, \(H_{\text{geminal-cis}}\)). \(^1^F\) NMR (CDCl\(_3\)) (Figure S3) \(\delta\) (ppm): −152.53 (d, \(J = 16.8\) Hz, 2F, \(F_{\text{ortho}}\)), −157.92 (s, \(J = 21.6\) Hz, 1F, \(F_{\text{para}}\)), −162.30 (dd, \(J = 16.8\) and 21.6 Hz, 2F, \(F_{\text{meta}}\)).

Synthesis of P(TBA=PFPA) Block Copolymer

Tert-butylicrylate (25 mL, 171 mmol), AIBN (41 mg, 0.25 mmol), and RAFT agent (600 mg, 2.5 mmol) were dissolved in 1,4-dioxane (85 mL), and the resulting clear yellow solution was purged for 1 h using \(N_2\) under gentle stirring. Polymerization was completed upon heating at 70 °C for 2 h, still under inert gas protection and slightly more vigorous stirring. The reaction was theromally quenched by pouring the flask in an ethanol/dry ice bath. Upon warm-up and thaw, the solution was precipitated in cold MeOH:H\(_2\)O (8:2, v:v). The recovered bright yellow polymer was purified further through 2 extra dissolution/precipitation cycles, dried under vacuum for 72 h at room temperature, using a rotary evaporator. The resulting clear pinkish liquid was subsequently purified through high-vacuum distillation.

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.1c00055.

Characterizations

Comprehensive instrumental and methodological descriptions are given in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.1c00055.

Experimental section, Figures S1–S45, and Tables S1–S6: NMR/FTIR spectra of precursors and/or MFGDs, size-exclusion chromatograms, TEM images, TGA curves, \(\zeta\) potential, XPS spectra, Mott–Schottky plots, graphitization control experiments, color gamuts, light diffusion and inner filter effects investigation, quantum yield, steady-state spectroscopies, Beer–Lambert plots, time-resolved spectroscopies data (TRES, TCSPC, fs-FLS, TPhotos, and TRFPS), lifetime distributions, wide-field fluorescence micrographs, and pictures of various MFGDs samples (PDF)

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Author Contributions

R.d.B. conducted chemical syntheses and associated physical-chemical, morphological, and structural analyses as well as the confocal microscopy study. A.L. conducted steady-state and time-resolved spectroscopic characterizations. All authors analyzed data and contributed to the redaction. X.L. and J.C. directed the research.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the A*STAR Singapore Research Attachment Programme (ARAP), the Natural Sciences and Engineering Research Council of Canada (NSERC) Discovery Program, and the Canada Research Chairs Program (CRCP). The authors warmly thank Paul-Ludovic Karsenti (Université de Sherbrooke, Québec) for extensive expertise and knowledge sharing regarding photophysics, Leonid Volkov (Centre Hospitalier Universitaire de Sherbrooke, Québec) for substantial expertise and valuable advice on microscopy, Kristijan Lulic and Pr. Jean Duhamel (Waterloo University, Ontario) for offering to conduct transient polarization fluorescence spectroscopy measurements and for comprehensive explanation on the technique, and Anna Capitaine (Université de Sherbrooke, Québec) for help regarding the synthesis and the understanding of the MFGDs.

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