Light-Emitting Multifunctional Maleic Acid-co-2-(N-(hydroxymethyl)acrylamido)succinic Acid-co-N-(hydroxymethyl)acrylamide for Fe(III) Sensing, Removal, and Cell Imaging

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ABSTRACT: The intrinsically fluorescent highly hydrophilic multifunctional aliphatic terpolymer, maleic acid (MA)-co-2-(N-(hydroxymethyl)acrylamido)succinic acid (NHASA)-co-N-(hydroxymethyl)acrylamide (NHMA), that is, 1, was designed and synthesized via C−C/N−C-coupled in situ allocation of a fluorophore monomer, that is, NHASA, composed of amido and carboxylic acid functionalities in the polymerization of two nonemissive MA and NHMA. The scalable and reusable intrinsically fluorescent biocompatible 1 was suitable for sensing and high-performance adsorptive exclusion of Fe(III), along with the imaging of Madin–Darby canine kidney cells. The structure of 1, in situ fluorophore monomer, aggregation-induced enhanced emission, cell-imaging ability, and superadsorption mechanism were studied via microstructural analyses using 1H/13C NMR, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, atomic absorption spectroscopy, Fourier transform infrared spectroscopy, ultraviolet–visible spectroscopy, thermogravimetric analysis, dynamic light scattering, high-resolution transmission electron microscopy, solid-state fluorescence, fluorescence lifetime, and fluorescence imaging, along with measuring kinetics, isotherms, and thermodynamic parameters. The location, electronic structures, and geometries of the fluorophore and absorption and emission properties of 1 were investigated using density functional theory and natural transition orbital analyses. The limit of detection and the maximum adsorption capacity were 2.45 × 10−7 M and 542.81 mg g−1, respectively.

INTRODUCTION

Recently, nonconventional intrinsically fluorescent biocompatible multifunctional multipolymers are of huge demand in sensing, removal, and biomedical applications. Additionally, the fluorescent polymers are employed for cellular imaging,1 DNA probing,2 biosensing,3 data security,4 and drug delivery.5 Earlier, although few nonconventional luminescent polymers have been reported,6 to date, a purely aliphatic intrinsically fluorescent multifunctional polymer bearing a branched tertiary amide fluorophore is scarcely reported.7 Therefore, we designed the synthesis of a nonconventional intrinsically fluorescent multifunctional terpolymer through multi C−C/ N−C-coupled solution polymerization in an aqueous environment, wherein the fluorophore monomer, that is, third monomer, was attached in situ via N−H functionalization.

Usually, amides emit clusteroluminescence, if a lone pair (n) of one carbonyl group interpenetrates the empty π∗ of another carbonyl.8 Moreover, extensive hydrogen bonding-driven closer association among the amide functionalities plays significant roles in elevating the fluorescence phenomena.7,9 Additionally, the branching units of the terpolymer bearing frequent aliphatic tertiary amides are expected to introduce the rigidity, leading to the high-performance nonconventional intrinsic fluorescence from purely aliphatic multipolymers.

For the precise detection of fluorophores and aggregation-induced enhanced emission (AIEE) in the polymer, density functional theory (DFT) and time-dependent DFT (TDDFT) are employed for measuring geometrical parameters and simulated absorption-emission properties, respectively.10 However, for the exact determination of fluorophore(s) and associated in depth analyses of the luminescent phenomena, natural transition orbital analyses (NTOs) are computed from the
equilibrium geometry of $S_1/S_2$ and $S_1/S_2 \rightarrow S_0$ transitions from occupied NTOs (hole) to unoccupied NTOs (electron). In general, strong blue/green emissions from polymers are substantiated by evaluating the hole−electron wave function overlap ($\sigma_{he}$) and separations ($\Delta r$) between holes and electrons.

Being an essential trace element of many enzymes and proteins, iron envisages major roles in metabolism and oxygen uptake. It is worth mentioning that although moderate concentration of Fe(III) is essential in living systems, the deficiency or overloading causes biological disorders including hepatic cirrhosis; endotoxemia; hereditary hemochromatosis; and Parkinson’s, Alzheimer’s, and Huntington’s diseases.
Thus, sensing and removal of Fe(III) are essential for the protection of human health, ecology, and environment. Importantly, Fe(III) imparts the quenching effect on fluorophores via paramagnetic quenching mechanism(s). Of the available methods for Fe(III) sensing, fluorescence spectroscopy is the smarter detection tool equipped with high sensitivity and selectivity, short response time, low detection limit, and low-cost. Earlier, maleic acid containing biocompatible copolymers have been reported for preliminary studies of hepatic cells and hemoglobin. Introduction of extra carboxylic acid functionality is expected to enrich the affinity toward protein and pH-responsive nature of the polymer. Though chemical oxidation, ion-exchange, biological treatment, adsorption, photocatalytic degradation, precipitation, ion exchange, membrane-based separation, complexation, and reverse osmosis have been employed for effective removal(s) of M(II/III), dyes, and organics for water decontamination, adsorption is widely employed because of availability, cost-effectiveness, and high efficiency of variable adsorbents.

Notably, fluorescent probes, nano particles (NPs), protein-based polymers, and NP-functionalized conjugated polymers have been employed in cell imaging. In this regard, the reported examples are mostly limited to conjugated polymers devoid of the biocompatible functionalities. Importantly, intrinsically fluorescent aliphatic polymers comprising amide functionalities are highly encouraged in imaging and biomedical applications. Thus, I is expected to interact sufficiently with cells in high-contrast imaging.

The nonconventional purely aliphatic intrinsically fluorescent multifunctional terpolymer has been synthesized employing two nonemissive monomers and N−H-functionalized C−C/N−C-coupled in situ attachment of a fluorescent tertiary amide monomer for three-in-one applications, such as Fe(III) sensing, high-performance removal of Fe(III), and Madin–Darby canine kidney (MDCK) cell imaging. The high-performance Fe(III) sensing and exclusion of Fe(III) have been attempted synthesizing 1 via in situ protrusion of the acrylamido-succinic acid monomer and selecting maleic acid, that is, unsaturated di-carboxylic acid, as one of the ex situ monomers.

Figure 2. (a) Absorption spectra and (b) emission spectra of 1 in CHCl₃, DMSO, and CH₃OH, (c) fluorescence spectra of 1 in CHCl₃ at variable wavelengths, (d) CHCl₃ and (e) DMSO at λex = 320 nm, (f) AIEE of 1 in DMSO + water at initial concentration = 200 μg mL⁻¹ and λex = 320 nm, (g) DLS of 1 in CHCl₃, CH₃OH, DMSO, and DMSO + water, (h) HRTEM image of 1, and (i) decay plots of 1 in CHCl₃ and DMSO.
RESULTS AND DISCUSSION

Synthesis of the Fluorescent Terpolymer. The fluorescent terpolymer was synthesized via solution polymerization involving NHMA + MA in water (Scheme 1). Initially, in a three-neck reactor, MA and NHMA were mixed, followed by the addition of \(\text{N,N’-methylenebisacrylamide (MBA)}\). Thereafter, the solution polymerization in water was initiated via slow additions of potassium persulfate (PPS) + sodium bisulfite (SBS) initiators. The as-synthesized terpolymer (Scheme 1) was swelled in 1:3 (v/v) methanol/water for removing unreacted monomers, oligomers, and other components, followed by drying in a vacuum oven for 24 h.

Characterization of the Fluorescent Terpolymer. The structure of 1 formed via multi C−C/N−C-coupled polymerization was confirmed from \(\text{−CH}_2−/\text{−CH}−\) peaks within 0.85−3.02 and 28.00−42.50 ppm in 1H and 13C NMR, respectively (Figure 1a,b). The protrusion of MA in 1 was confirmed from the \(\text{−COO}−\) peak at 183 ppm, supported from the 1H NMR peak of \(\text{−COOH}−\) at 9.74 ppm. In 1, NHMA was confirmed from \(\text{−CON−CH}_2\text{OH}−\) and \(\text{−CON−CH}_2\text{OH}−\) peaks at 5.72 and 64.20 ppm, respectively. Most importantly, the in situ attachment of the tertiary amide fluorophore monomer, that is, NHASA, was inferred from \(\text{−CON(−CH}_2\text{OH)}−\text{−CH}−\) and \(\text{−CON(−CH}_2\text{OH)}−\text{−CH}−\) peaks at 4.84 \(\text{cm}^{-1}\) and 69.90 ppm, respectively (Figure 1a,b).

In FTIR, the protrusions of MA and NHMA in 1 were confirmed from \(\text{−COO}−\) asym. str. of MA at 1655/1622 cm\(^{-1}\), along with \(\text{−CH}_3−\text{O} \text{def.} \text{and hydrogen-bonded O−H def.}\) of NHMA at 1016 and 1396 cm\(^{-1}\), respectively (Figure 1c). Importantly, the in situ attached NHASA confirmed earlier in NMR analyses was supported by C−N−C asym. str. of tertiary amides at 861 cm\(^{-1}\) (Figure 1c).

In this regard, the in situ attachment of NHASA and ex situ added MA and NHMA were confirmed from N 1s, O 1s, and C 1s binding energies (BEs) in XPS of 1 (Figure 1d–f and Table S2). The coexistences of secondary and tertiary amides in 1 were realized from N 1s BEs of \(\text{−CON}−\) and \(\text{−CONH}−\) functionalities at 398.73 and 399.30 eV, respectively (Figure 1d). Additionally, in 1, \(\text{−C==O}, \text{−COO}−\), and \(\text{−OH}\) were confirmed from BEs at 530.35, 531.24, and 531.88 eV, respectively (Figure 1e). In this regard, \(\text{−CH}_3/\text{−CH}−/\text{−CH}−/\text{−C−N/C−OH/C−O},\) and \(\text{−CONH}−/\text{−CON}−/\text{−C==O}\) were confirmed from BEs at 283.78, 284.73, and 286.74 eV, respectively (Figure 1f).

From thermogravimetric (TG) analysis of 1, moisture loss from hydrophilic functionalities was completed within 150 °C. Thereafter, 12 wt % loss within 151−300 °C was ascribed to the removal of water molecules from closely pendent dicarboxylic acid moieties in 1, forming cyclic anhydrides (Figure S1). The accelerated degradation beyond 300 °C could be related to the decomposition of remaining carboxylate functionalities of 1. Beyond 390 °C, the decompositions of anhydride rings and backbone of 1 superimposed. In fact, the overall thermal degradation of 1 completed at 540 °C resulting in the 3 wt % residue in the thermogram. Thus, the in situ attached aliphatic amide-fluorophore and associated branching and clusters formed via elevated hydrogen bonding encouraged the intrinsic fluorescence of 1. However, the in situ protruded tertiary amide fluorophore monomer, that is, NHASA, imparted rigid terpolymer networks, causing enriched photostructural properties.
Photophysical Studies. For 1, the absorption and emission spectra were recorded in solvents of variable polarities. Herein, the absorption peaks at 241, 257, and 203 nm in CHCl₃, DMSO, and CH₃OH, respectively, appeared via $\pi \to \pi^*$ transitions (Figure 2a). The broad shoulders at 274, 276, and 222 nm in CHCl₃, DMSO, and CH₃OH, respectively, originated via $n \to \pi^*$ transitions (Figure 2a). Additionally, the emission peaks of 1 appeared at 430, 434, and 424 nm in CHCl₃, DMSO, and CH₃OH, respectively (Figure 2b). In the emission spectra, bathochromic shifts in more polar solvents were attributed to the gradual drop of energy differences between excited and ground states. Importantly, the emission maxima appeared at a lower wavelength in MeOH compared to DMSO of greater polarity. Thus, polarity merely cannot account for the weak solvatochromic ability of 1. In this regard, the extent of hydrogen bonding definitely plays a leading role in the photophysics of 1 in the polar protic solvent. In the fluorescence spectra of 1, $\lambda_{em}$ remained unchanged at $\lambda_{ex} = 300, 320, 340, 360, 380,$ and 400 nm. Herein, the intensities varied with the $\lambda_{ex}$ and the maximum intensity was observed at 380 nm (Figure 2c). The fluorescence intensities of 1 in CHCl₃ and DMSO dropped gently via gradual decrease in concentrations (Figure 2d,e). Though the additions of DMSO in 1 + DMSO solutions gently decreased the fluorescence intensities, the intensities elevated rapidly by increasing water volume fractions (Figure 2f). Herein, the aggregation of 1 created the rigid structure through restrained molecular motions. In this regard, the higher volume fractions of more polar water decreased the solubilities of 1 in DMSO + water, as solubility of 1 was higher in less polar DMSO compared to water. The emission-maximum was noted at 16:84 (v/v) water/DMSO solution. The fluorescence intensities diminished upon further additions of water into the 1 + DMSO solutions. The extents of aggregations, that is, sizes/orders of aggregates, in DMSO + water solutions were measured by the dynamic light scattering (DLS), substantiated from high-resolution transmission electron microscopy (HRTEM) photomicrographs (Figure 2g,h). The intensity average hydrodynamic diameters, that is, $D_{ho}$ of 1 in solutions increased from 239 to 317 nm (Figure 2g). Additionally, the effects of external stimuli, such as pH and temperature, on the photophysics of 1 were studied, from which the fluorescence intensities decreased slightly with increasing temperatures (Figure S2a). In contrast, the intensities increased significantly with increasing pH from 2.0 to 12.0 (Figure S2b). Additionally, the average lifetimes of 1 in CHCl₃ and DMSO were calculated as 0.98 and 1.0 ns, respectively (Figure S2a). In the solid state, the intense blue and green fluorescence of 1 was confirmed from fluorescence imaging recorded through DAPI (i.e., 461 nm) and FITC (i.e., 519 nm) channels, respectively (Figure S2c,d), related to intra- and inter-chain n–$\pi$ interactions of fluorophores.\(^{31}\)

Computational Studies. The geometries of ground-state ($S_0$), first excited-state ($S_1$), and geometrical parameters of 1...
were envisaged in Figure 3a. The excitation from S0 to S1 resulted in the noticeable changes in bond lengths and bond angles in two positions of the in situ attached NHASA moiety. The amodic >C=O length of the NHASA moiety increased from 1.23 Å in S0 to 1.40 Å in S1. Additionally, the amodic C—N length of NHASA increased from 1.38 Å in S0 to 1.42 Å in S1. Additionally, the changes in O=C−N and C−C=O from 119 and 117° in S0 to 111 and 112° in S1, respectively, supported planar to pyramidal structural alteration of the amide-carbonyl center of NHASA (Figure 3a). Notably, in S0/S1 of 1, hydrogen bond lengths between −NHCH2O and >CH2COOH were measured within 1.94–1.97 Å, signifying marginal deviation from the Franck–Condon principle. Herein, the strong emissive nature of 1 was confirmed from the decrease in the HOMO–LUMO energy gap, that is, $\sigma_{he}$ and the separation between the centroids of hole and electron distribution, that is, $\Delta r$, for the lowest singlet states were calculated using NTO analysis based on the singular value decomposition of the 1-particle transition density matrix.32 For 1, $\sigma_{he}$ and $\Delta r$ were 0.058 and 1.315 Å for S1 and 0.231 and 4.120 Å for S2 (Figure 3c), in which smaller $\sigma_{he}$ and larger $\Delta r$ substantiated the stronger charge-transfer ability of 1.

**Turn-Off Fe(III) Sensor.** The binding affinities of 1 with metal ions, such as K+, Ag(I), Ca(II), Cu(II), Fe(II), Ni(II), Zn(II), Cd(II), Hg(II), Cr(III), Fe(III), Sb(III), and Bi(III), were explored at 298 K and pH within 7.0–8.0. Herein, 1 was excited at 320 nm, and the emission was recorded within 340–600 nm employing 5 and 8 nm slit-widths for the source and detector, respectively. In the fluorescence titration, 2.0×10$^{-4}$ M metal ions were added each time in a quartz cuvette containing 2.6 mL 80−100 μg mL$^{-1}$ 1 in 6:1 (v/v) DMSO/H$_2$O (Figure 4a). From the results, the fluorescence quenching efficiency ($\eta$) was calculated using eq 1.33

$$\eta = (I_0 - I)/I_0 \times 100$$

Importantly, only Fe(III) envisaged the maximum fluorescence quenching over other metal ions (Figure 4a), confirmed from the additions of 25.0×10$^{-4}$ M metal ions each to the solutions of 1 + DMSO/H$_2$O. In this regard, the decrease in fluorescence intensities via incremental additions of Fe(III) into solution of 1 confirmed the stable complexation of
Fe(III) with 1 (Figure 4b). The addition of $2.65 \times 10^{-3}$ M Fe(III) in solution of 1 quenched the fluorescence intensity to 98.07%, whereas for other metal ions, the quenching efficiencies were measured within 0−63%. Herein, the time required for quenching was noted within 1 s. At low Fe(III) concentrations, the linear nature of quenching (Figure 4b−d) and the elevated quenching at higher Fe(III) concentrations indicated static or static + dynamic quenching mechanism in the turn-off Fe(III) sensing of 1.34 Additionally, at low Fe(III) concentrations, the static quenching at the ground state of the Fe(III)-1 complex was confirmed from UV−vis analyses (Figure 5a), inferred from unaltered fluorescence lifetimes of the Fe(III)-1 complex (Figure 5b). In contrast, alterations of lifetimes at higher Fe(III) concentrations confirmed the static + dynamic quenching mechanism in the turn-off Fe(III) sensing of 1 (Figure 5c). The SV quenching constant ($K_{SV}$), that is, $2.22 \times 10^3$ M$^{-1}$, confirmed the greater binding affinity of 1 with Fe(III) (Figure 4d). From the fluorescence titration plot using 0−4 μM Fe(III), the limit of detection (LOD) was $2.45 \times 10^{-7}$ M (S/N = 3) (Figure 5d), which was much lesser compared to the values reported to date.35

Adsorption Isotherms, Kinetics, and Thermodynamics.

The equilibrium adsorption data were fitted to three different isotherm models, that is, Langmuir, Freundlich, and BET (eqs 2−4), of which Langmuir model (Figure 6a) fitted the best (Table 1). In low ppm, photophysical studies envisaged the highest binding affinity of 1 with Fe(III). Importantly, even in high ppm, the excellent removal efficiency was further confirmed from the very high $q_{\text{max}}$ of 1, that is, 542.81 mg g$^{-1}$. The higher binding affinity of Fe(III) with O-donor ligands resulted in the elevated $q_{\text{max}}$. The adsorption of

| models | parameters | Fe(III) temperature (K) | 293 | 303 | 313 | 323 |
|--------|------------|------------------------|-----|-----|-----|-----|
| Langmuir | $q_{\text{max}}$ (mg g$^{-1}$)/pH/$C_0$ (ppm) | 563.81/7/100−500 | 542.81/7/100−500 | 524.05/7/100−500 | 490.06/7/100−500 |
| | $k_1$ (L mg$^{-1}$) | 0.0782 | 0.0659 | 0.0401 | 0.0366 |
| | $R^2/F$ | 0.9993/12957.03 | 0.9990/9014.95 | 0.9910/4625.45 | 0.9985/6460.94 |
| | $q_{\text{cal}}$ (mg g$^{-1}$)/pH/$C_0$ (ppm) | 505.09/7/500 | 451.43/7/500 | 401.94/7/500 | 365.34/7/500 |
| | $q_{\text{exp}}$ (mg g$^{-1}$) | 483.29 ± 14.50 | 440.47 ± 13.21 | 395.17 ± 12.87 | 360.85 ± 10.83 |
| | $k_2$ (g mg$^{-1}$ min$^{-1}$) | $1.40 \times 10^{-4}$ | $1.84 \times 10^{-4}$ | $2.45 \times 10^{-4}$ | $3.30 \times 10^{-4}$ |
| | $R^2/F$ | 0.9843/4327.57 | 0.9986/41230.17 | 0.9997/175615.74 | 0.9997/190000.49 |
Fe(III) was spontaneous as a separation factor, that is, $R_L$ (eq 5), varies from 0 to 1.

$$q_e = q_{\text{max}} \frac{k_i C_e}{1 + k_i C_e}$$  \hspace{1cm} (2)

$$q_e = k_p C_{e}^{1/n}$$  \hspace{1cm} (3)

$$q_e = q_{\text{RET}} \frac{(1 - k_1 C_e)(1 - k_2 C_e + k_1 C_e)}{1 - k_2 C_e}$$  \hspace{1cm} (4)

Here, $q_{\text{max}}$, $n$, and $q_{\text{RET}}$ and $k_i$, $k_p$, $k_1$, and $k_2$ are isotherm parameters and isotherm constants, respectively.

$$R_L = \frac{1}{1 + k_i C_0}$$  \hspace{1cm} (5)

Additionally, the adsorption data were fitted to pseudo-first- and pseudo-second-order kinetics models (Figure 6b and Table 1), of which the better fitting of the pseudosecond-order kinetics equation (eq 7) compared to pseudofirst-order kinetics equation (eq 6) supported the chemical attachment of Fe(III) with 1 (Table 1) via ionic and coordinative interactions between Fe(III) and O-donor functionalities, that is, -COOH and -COO⁻. Additionally, the activation energy ($E_a$) of adsorption was 22.49 kJ mol⁻¹, supported the prevalence of chemisorption (Figure 6c). The spontaneity of the chemisorption was understood from $-\Delta G^0$ data (eq 9).

$$q_t = q_f [1 - \exp(-k_f t)]$$  \hspace{1cm} (6)

$$q_t = q_f \left(1 - \frac{1}{1 + k_f q_f t}\right)$$  \hspace{1cm} (7)

$$\ln k_2 = \ln k_0 - \frac{E_1}{RT}$$  \hspace{1cm} (8)

$$\Delta G^0 = -RT \ln k_d$$  \hspace{1cm} (9)

The distribution coefficient ($k_d$) is defined as the ratio of Fe(III) concentrations in solid to liquid phases at equilibrium (eq 10).

$$k_d = \frac{q_e}{C_e}$$  \hspace{1cm} (10)

$$\ln k_d = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$  \hspace{1cm} (11)

The exothermicity of adsorption was realized from the negative $\Delta H^0$ (Table 2) calculated using equation (eq 11), whereas the positive $\Delta S^0$ suggested a fair binding affinity of Fe(III) with 1 (Figure 6d).

**Characterization of Fe(III)-1.** From Figure 7a, substantial alterations in characteristic -COO⁻ asym. str. and -COO⁻ sym. str. were observed in Fe(III)-1. The -COO⁻ asym. str. and -COO⁻ sym. str. peaks appeared at 1655/1622 and 1458/1396 cm⁻¹ in 1 shifted to 1649 and 1450/1382 cm⁻¹ in Fe(III)-1, respectively. Importantly, substantial enrichment of -COO⁻ functionality, that is, O-donor, in Fe(III)-1 was ascribed to the increase in intensity of -COO⁻ sym. str. at 1450 cm⁻¹, supported from the disappearance of O–H def. of -COOH at 1364 cm⁻¹ in 1. Additionally, the mutual O–H…

### Table 2. Adsorption Thermodynamics Parameters for Fe(III)-1

| $C_0$ (ppm) | $T$ (K) | $-\Delta G^0$ (kJ mol⁻¹) | $-\Delta H^0$ (kJ mol⁻¹) | $-\Delta S^0$ (J mol⁻¹ K⁻¹) |
|-------------|---------|--------------------------|--------------------------|---------------------------|
| 100         | 293     | 8.78                     | 28.80                    | 68.58                     |
| 300         | 8.04    | 9.40                     | 28.80                    | 68.58                     |
| 313         | 7.01    | 11.76                    | 28.80                    | 68.58                     |
| 323         | 6.87    | 12.46                    | 28.80                    | 68.58                     |
| 200         | 7.53    | 19.64                    | 41.38                    |                           |
| 300         | 5.98    | 9.40                     | 11.76                    |                           |
| 313         | 5.83    | 10.55                    | 20.13                    |                           |
| 323         | 5.67    | 12.46                    | 20.13                    |                           |
| 400         | 5.09    | 8.73                     | 12.46                    |                           |
| 303         | 4.95    | 9.45                     | 11.76                    |                           |
| 313         | 4.82    | 10.55                    | 20.13                    |                           |
| 323         | 4.72    | 12.46                    | 20.13                    |                           |
| 500         | 4.65    | 10.55                    | 20.13                    |                           |
| 303         | 4.45    | 9.45                     | 11.76                    |                           |
| 313         | 4.23    | 10.55                    | 20.13                    |                           |
| 323         | 4.05    | 12.46                    | 20.13                    |                           |

N–H hydrogen-bonding peak at 3283 cm⁻¹ reduced substantially in Fe(III)-1, inferring the conversion of -COOH to -COO⁻. Additionally, participation of amide functionalities in complexation was confirmed from peaks of >NH⁻ and >C=NH⁺ at 1831, 2052, 2162, 2287, and 2323 cm⁻¹, along with the disappearance of C–N–C asym. str. of -CON< at 861 cm⁻¹, inferred from -C(O<)=N< at 400.92 eV in XPS (Figure 7b). The weak ionic binding affinity of Fe(III) with amide functionalities was realized from the marginal increase in N 1s BE from 398.73/399.30 eV in 1 to 398.92/399.51 eV in Fe(III)-1 (Figures 7d and 7b). However, the intimate coordinate bonding of the O-donor with Fe(III) was realized from the significant increase in O1s BEs of >C=O, -COO⁻, and O–H from 530.35, 531.24, and 531.88 to 530.75, 531.85, and 532.66 eV (Figures 1e and 7c). The binding through -COO⁻, -CONH–, and -CON< functionalities decreased the electron density around the C-center, substantiated through the increase in BEs from 283.78, 284.73, and 286.74 eV in 1 to 284.27, 285.29, and 287.16 eV in Fe(III)-1 (Figures 1f and 7d). Additionally, the interaction of 1 with Fe(III) was realized from TG analysis, in which elevated thermal stability of Fe(III)-1 compared to 1 within 151–390 °C envisaged astringed anhydride formation in the presence of Fe(III) ions. Beyond 390 °C, the lesser thermal stability of Fe(III)-1 compared to 1 was related to the absence of cyclic anhydrides. Thus, a sharp degradation continued up to 490 °C resulted in 24 wt % residue of Fe(III) salts, correlating the higher AC, that is, 542.81 mg g⁻¹ (Figure 7e).

Cell Viability and Cell Imaging. From the MTT assay, 1 was noncytotoxic to the MDCK cell, substantiated from p < 0.05 for the cells treated with 0.2, 0.5, 1.0, and 1.5 μg mL⁻¹ solutions of 1 (Figure 8a,b). Additionally, 1 was biocompatible, as more than 95% MDCK cells continued to have the cell morphologies (Figure 8a). For fluorescence imaging, the MDCK cell was naturally developed on a poly L-lysine-coated coverslip for proper seeding. Thereafter, the seeded cells were treated with 0.2 μg μL⁻¹ 1 and incubated for 50 min at 37 °C.
These cells were fixed with 4:96 (v/v) paraformaldehyde/water for 2 h at 37 °C followed by washing in 1× PBS three times. The fluorescence imaging of both control and treated cells was measured through DAPI (i.e., 461 nm) and FITC (i.e., 519 nm) channels and mounting the cell on a glass slide (Figure 8c–f). The cell and nuclear membrane permeabilities of intrinsically fluorescent-1 and the retention of cell morphologies confirmed the suitability of 1 for cell imaging of normal cells.

**CONCLUSIONS**

This work reports the synthesis of purely aliphatic intrinsic blue and green light-emitting 1 via C−C/N−C-coupled in situ attachment of a fluorophore monomer in solution polymerization of two nonfluorescent monomers. The N−H-functionalized in situ protrusion of the fluorophore monomer has been confirmed from NMR and XPS peaks of the tertiary amide. The smaller H−Li nS1 compared to S0, along with smaller $\sigma$ and larger $\Delta r$, infer the n → π* emissive charge-transfer in 1. The AIEEs of 1 has=ve been substantiated from HRTEM, DLS, and photophysical studies. The scalable and reusable pH-

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**Figure 7.** (a) FTIR spectrum of Fe(III)-1, XPS spectra of (b) N 1s, (c) O 1s, and (d) C 1s for Fe(III)-1, and (e) TG analyses of 1 and Fe(III)-1.

**Figure 8.** (a) Bright-field image of the MDCK cell, (b) cell viability of MDCK cells treated with 1, images of MDCK cell through (c) DAPI and (e) FITC channels, and images of MDCK cells treated with 1 through (d) DAPI and (f) FITC channels.
responsive biocompatible fluorescent terpolymer envisages the excellent Fe(III)-sensing at lower LOD, high-performance removal of Fe(III), excellent cell viability, and high-contrast cell imaging on normal MDCK cells. The new method for strategic synthesis of intrinsically fluorescent multifunctional 1 should be broadened for the syntheses of other purely aliphatic intrinsically fluorescent biocompatible multipolymers for prospective sensing, removal, and biomedical applications.

**EXPERIMENTAL SECTION**

**Materials.** CH$_3$OH, CHCl$_3$, and DMSO of the HPLC grade were purchased from Sigma-Aldrich. HCl, NaOH, MA, NHMA, MBA, PPS, SBS, AgNO$_3$, CaCl$_2$, KCl, Ni(NO$_3$)$_2$, 6H$_2$O, Cr(NO$_3$)$_3$,9H$_2$O, Cu(NO$_3$)$_2$, FeCl$_3$, FeCl$_2$, HgCl$_2$, CdCl$_2$, Zn(NO$_3$)$_2$,6H$_2$O, SbCl$_3$, Co(NO$_3$)$_2$,6H$_2$O, and Bi(NO$_3$)$_3$ of analytical grades were purchased from Merck.

**Synthesis of the Fluorescent Terpolymer.** The fluorescent terpolymer was synthesized by solution polymerization involving NHMA + MA in water (Scheme 1). Initially, in a three-neck reactor, 30 mL 0.0443 mol NHMA and 10 mL 0.0044 mol MA were mixed at 600 rpm, followed by adding 5 mL 0.2594 mmol MBA. Thereafter, the solution polymerization in water was initiated via gradual additions of 10 mL 0.0925 + 0.2402 mmol PPS + SBS redox initiators. The as-prepared terpolymer (Scheme 1) was allowed to swell in 1:3 (v/v) methanol/water solution for removing unreacted monomers, oligomers, and other components, followed by drying under vacuum for 24 h.

**Characterization.** The terpolymer was characterized using techniques summarized in Table S6. Origin 9.0 and ChemDraw Ultra 12.0 were used for graphics-based analyses and drawing chemical structures, respectively.

**Computational Details.** The spin-restricted formalism at the B3LYP/6-31G(d) level of DFT was employed for the optimization of S$_0$ geometries of 1, using Gaussian 09 package. The frequency calculations were done to test the optimized structures relating to the minima on potential energy surfaces. To find the vertical excited energies, S$_1$ structures were optimized via TDDFT at the B3LYP/6-31G(d) level. Additionally, long-range functional CAM-B3LYP, oB97XD, and hybrid functional PBE0 were employed for computing vertical excitation energies. Fluorescence energies were computed from the lowest excited-state optimized structures. The first twenty S$_1$ → S$_0$ transitions were evaluated employing TD-B3LYP/6-31G(d). Additionally, for exploring exact pictures of excited states, NTO analyses were performed to represent the compact orbital.

**Calculation of the Average Lifetime.** The average lifetimes of 1 and Fe(III)-1 were calculated using the method reported elsewhere.

**Cell Lines and MTT Assay.** The MDCK cell was purchased from ATCC. The cell was cultured in the Eagle’s minimal essential medium, supplemented with 1:99 (v/v) penicillin streptomycin/water solution and 10% (v/v) fetal bovine serum in 95:5 (v/v) air/CO$_2$ within a humidified incubator at 37 °C. In a 96-well plate, 10$^4$ MDCK cells were plated and incubated overnight for seeding at a standard dose of radiation and compounds. Thereafter, MDCK cells were treated with 1 of variable concentrations. After 72 h incubation, MTT assay was done for determining the cell viability. For each experiment, the assay was performed thrice independently. The decrease in viability was directly proportional to the cytotoxic effect of 1. The viability of cell was calculated from the following equation:

\[
\text{% cell viability} = \frac{(\text{absorbance})_{\text{sample}}}{(\text{absorbance})_{\text{control}}} \times 100
\]  

(12)

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03536.

TG analysis of 1; effect of temperature and pH on fluorescence intensity of 1 and fluorescence images of 1 through DAPI (i.e., 461 nm) and FITC (i.e., 519 nm) channels MOs of 1 in S$_0$ and S$_1$; FTIR and XPS analyses of 1 and Fe(III)-1; orbital compositions of S$_0$ and S$_1$ for 1; absorbance and emission data of 1; and coordinates of 1 in S$_0$ and S$_1$ (PDF)

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Notes
The authors declare no competing financial interest.

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REFERENCES
(1) Xiong, H.-M.; Xu, Y.; Ren, Q.-G.; Xia, Y.-Y. Stable Aqueous ZnO@Polymer Core-shell Nanoparticles with Tunable Photoluminescence and Their Application in Cell Imaging. J. Am. Chem. Soc. 2008, 130, 7522–7523.
(2) Liu, B.; Bazan, G. C. Homogeneous Fluorescence-based DNA Detection with Water-soluble Conjugated Polymers. Chem. Mater. 2004, 16, 4467–4474.
(3) (a) Zhang, C.; Yuan, Y.; Zhang, S.; Wang, Y.; Liu, Z. Biosensing Platform Based on Fluorescence Resonance Energy Transfer from Upconverting Nanocrystals to Graphene Oxide. Angew. Chem., Int. Ed. 2011, 50, 6851–6854. (b) Ramanathan, K.; Bangar, M. A.; Yun, M.; Chen, W.; Myung, N. V.; Mulchandani, A. Bioaffinity Sensing Using Biologically Functionalized Conducting-polymer Nanowire. J. Am. Chem. Soc. 2005, 127, 496–497.
(4) (a) Chen, D.; Cui, C.; Tong, N.; Zhou, H.; Wang, X.; Wang, R. Water-soluble and Low-toxic Ionic Polymer Dots as Invisible Security Ink for Multi Stage Information Encryption. ACS Appl. Mater. Interfaces 2019, 11, 1480–1486. (b) Wang, H.; Ji, X.; Li, Z.; Zhu, C. N.; Yang, X.; Li, T.; Wu, Z. L.; Huang, F. Preparation of a White-light-emitting Fluorescent Supramolecular Polymer Gel with a Single Chromophore and Use of the Gel to Fabricate a Protected Quick Response Code. Mater. Chem. Front. 2017, 1, 167–171.
(5) (a) Chen, Y.; Wilbon, P. A.; Zhou, J.; Nagarkatti, M.; Wang, C.; Chu, F.; Tang, C. Multifunctional Self-fluorescent Polymer Nanogels for Label-free Imaging and Drug Delivery. Chem. Commun. 2013, 49, 297–299. (b) Zhu, H.; McShane, M. J. Loading of Hydrophobic Materials into Polymer Particles: Implications for Fluorescent Nanosensors and Drug Delivery. J. Am. Chem. Soc. 2005, 127, 13448–13449. (c) Mitra, S.; Sasmal, H. S.; Kundu, T.; Kandambeth, S.; Illath, K.; Díaz Díaz, D.; Banerjee, R. Targeted Drug Delivery in Covalent Organic Nanosheets (CONs) via Sequential Postsynthetic Modification. J. Am. Chem. Soc. 2017, 139, 4513–4520.
(6) (a) Lee, W. I.; Bae, Y.; Bard, A. J. Strong Blue Photoluminescence and ECL from OH-Terminated PAMAM Dendrimers in the Absence of Gold Nanoparticles. J. Am. Chem. Soc. 2004, 126, 8358–8359. (b) Sun, M.; Hong, C.-Y.; Pan, C.-Y. A Unique Aliphatic Tertiary Amine Chromophore: Fluorescence, Polymer Structure, and Application in Cell Imaging. J. Am. Chem. Soc. 2012, 134, 20581–20584. (c) Lu, H.; Feng, J.; Li, S.; Zhang, J.; Lu, H.; Feng, S. Unexpected Strong Blue Photoluminescence Produced from the Aggregation of Unconventional Chromophores in Novel Siloxane–poly(amoidoamine) Dendrimers. Macromolecules 2015, 48, 476–482.
(7) Ye, R.; Liu, Y.; Zhang, H.; Su, H.; Zhang, Y.; Xu, L.; Hu, R.; Kwok, R. T. K.; Wong, K. S.; Lam, J. W. Y.; Goddard, W. A.; Tang, B. Z. Non- conventional Fluorescent Biogenic and Synthetic Polymers without Aromatic Rings. Polym. Chem. 2017, 8, 1722–1727.
(8) Zhou, X.; Luo, W.; Nie, H.; Xu, L.; Hu, R.; Zhao, Z.; Qin, A.; Tang, B. Z. Oligo(maleic anhydride): A Platform for Unveiling the Mechanism of Clusteroluminescence of Non- aromatic Polymers. J. Mater. Chem. C 2017, 5, 4775–4779.
(9) Li, W.; Che, C.; Pang, J.; Cao, Z.; Jiao, Y.; Xu, J.; Ren, Y.; Li, X. Autofluorescent Polymers: 1H,1H,2H-Perfluorodecanol Grafted Poly(styrene-b-acrylic acid) Block Copolymers without Conventional Fluorophore. Langmuir 2018, 34, 5334–5341.
(10) (a) Vallan, L.; Urrilolabeta, E. P.; Ruizpérez, F.; Matxin, J. M.; Canton-Vitoria, R.; Tagnatarchis, N.; Benito, A. M.; Maser, W. K. Supramolecular-enhanced Charge Transfer within Entangled Polyamide Chains as the Origin of the Universal Blue Fluorescence of Polymer Carbon Dots. J. Am. Chem. Soc. 2018, 140, 12862–12869.
(b) Tirado-Rives, J.; Jorgensen, W. L. QM/MM Calculations for the Cl− + CH3Cl SN2 Reaction in Water Using CMS Charges and Density Functional Theory. J. Phys. Chem. A 2019, 123, 5713–5717. (c) Gan, L.; Gao, K.; Cai, X.; Chen, D.; Su, S.-J. Achieving Efficient Triple Exciton Utilization with Large ΔEgs and Nonobvious Delayed Fluorescence by Adjusting Excited State Energy Levels. J. Phys. Chem. Lett. 2018, 9, 4725–4731.
(11) Ling, S.; Schumacher, S.; Galbraith, I.; Paterson, M. J. Excited-state Absorption of Conjugated Polymers in the Near Infrared and Visible: A Computational Study of Oligofluorenes. J. Phys. Chem. C 2013, 117, 6889–6895.
(12) Fan, X.; Li, C.; Wang, Z.; Wei, Y.; Duan, C.; Han, C.; Xu, H. Enhancing Reverse Intersystem Crossing via Secondary Acceptors: Toward Sky-blue Fluorescent Diodes with 10-Fold Improved External Quantum Efficiency. ACS Appl. Mater. Interfaces 2019, 11, 4185–4192.
(13) (a) Zhang, Y.; Li, X.; Gao, L.; Qiu, J.; Heng, L.; Tang, B. Z.; Jiang, L. Sulfonated Photonic Crystal Films as Effective Fluorescence Sensor for Fe3+ and Hg2+. ChemPhysChem 2014, 15, 507–513. (b) Wang, J.; Jiang, M.; Yan, L.; Peng, R.; Huangfu, M.; Guo, X.; Li, Y.; Wu, P. Multifunctional Luminescent Eu(III)-based Metal-organic Framework for Sensing Methanol and Detection and Adsorption of Fe(III) Ions in Aqueous Solution. Inorg. Chem. 2016, 55, 12660–12668.
(14) Zheng, M.; Tan, H.; Xie, Z.; Zhang, L.; Jing, X.; Sun, Z. Fast Response and High Sensitivity Europium Metal Organic Framework Fluorescent Probe with Chelating Terpyridine Sites for Fe3+. ACS Appl. Mater. Interfaces 2013, 5, 1078–1083.
(15) (a) Zhou, W.; Saran, R.; Liu, J. Metal Sensing by DNA. Chem. Rev. 2017, 117, 8272–8325. (b) Zhou, W.; Zhang, Y.; Ding, J.; Liu, J. In Vitro Selection in Serum: RNA-cleaving DNAzymes for Measuring Ca2+ and Mg2+. ACS Sens. 2016, 1, 600–606. (c) Zhou, W.; Vazin, ...
sulfur-filler of Rubber Membranes: Systematic Optimization and Comprehensive Mechanistic Study. Korean J. Chem. Eng. 2017, 34, 1416–1434. (e) Singh, N. R.; Karmakar, M.; Chattopadhyay, P. K.; Roy, S.; Deb, M.; Mondal, H.; Mahapatra, M.; Dutta, A.; Mitra, M.; Roy, J. S. D. Structures, Properties, and Performance-relationships of Polymeric Membranes for Pervaporative Desalination. Membranes 2019, 9, 38. (f) Singh, N. R.; Ray, S. K. Removal of Pyridine from Water by Pervaporation using Crosslinked and Filled Natural Rubber Membranes. J. Appl. Polym. Sci. 2012, 124, E99–E107. (g) Singha, N. R.; Ray, S.; Ray, S. K.; Konar, B. B. Removal of Pyridine from Water by Pervaporation using Filled SBR Membranes. J. Appl. Polym. Sci. 2011, 121, 1330–1334.

(22) Asnavandi, M.; Zhao, C. Hydrogen Bubble-assisted Electrodeposition of Metal Nanoparticles from Protonic Ionic Liquids for Electrocatayst. ACS Sustainable Chem. Eng. 2017, 5, 85–89.

(23) Weber, C. C.; Wood, G. P. F.; Kunov-Kruse, A. J.; Nmagu, D. E.; Trout, B. L.; Myerson, A. S. Quantitative Solution Measurement for the Selection of Complexing Agents to Enable Purification by Impurity Complexation. Cryst. Growth Des. 2014, 14, 3649–3657.

(24) Ikehata, K.; Zhao, Y.; Kulkarni, H. V.; Li, Y.; Snyder, S. A.; Ishida, K. P.; Anderson, M. A. Water Recovery from Advanced Water Pervaporation Facility Reverse Osmosis Concentrate by Photobiological Treatment followed by Secondary Reverse Osmosis. Environ. Sci. Technol. 2018, 52, 8588–8595.

(25) (a) Karmakar, M.; Mahapatra, M.; Dutta, A.; Chattopadhyay, P. K.; Singh, N. R. Fabrication of Semisynthetic Collagen Materials for Membrane/ Synergetic Adsorption: A Model Approach of Determining Dye Allocation by Systematic Characterization. Int. J. Biol. Macromol. 2017, 102, 438–456. (b) Singh, N. R.; Dutta, A.; Mahapatra, M.; Roy, J. S. D.; Mitra, M.; Deb, M.; Chattopadhyay, P. K. In Situ Attachment of Acylaminol Sulfonic Acid-based Monomer in Terpolymer Hydrogel Optimized by Response Surface Methodology for Individual and/or Simultaneous Removal(s) of M(III) and Cationic Dyes. ACS Omega 2019, 4, 1763–1780.

(26) (a) Passos, S. T. A.; Correa, J. R.; Soares, S. L. M.; da Silva, W. A.; Neto, B. A. D. Fluorescent Peptoids as Selective Live Cell Imaging Probes. J. Org. Chem. 2016, 81, 2646–2651. (b) Chen, Z.; Wu, P.; Cong, R.; Xu, N.; Tan, Y.; Tan, C.; Jiang, Y. Sensible Conjugated-polymer-based Fluorescent ATP Probes and their Application in Cell Imaging. ACS Appl. Mater. Interfaces 2016, 8, 3567–3574. (c) Wang, T.; Yin, P.; Yang, Y.; Yin, W.; Zhang, S.; Yang, M.; Qiu, Y.; Ma, Y.; Lei, Z.; Ma, H. Effect of Element Indone on the Cell Membrane Transportability of Fluorescent Polymers and Lysosome-targeted Cell Imaging. ACS Sustainable Chem. Eng. 2019, 7, 6295–6303.

(27) (a) Yang, Y.; Wang, X.; Cui, Q.; Cao, Q.; Li, L. Self-assembly of Fluorescent Organic Nanoparticles for Iron(III) Sensing and Cellular Imaging. ACS Appl. Mater. Interfaces 2016, 8, 7440–7448. (b) Chen, J.; Zhong, W.; Tang, Y.; Wu, Z.; Li, Y.; Yi, P.; Jiang, J. Amphiphilic BODIPY-based Photoswitchable Fluorescent Polymeric Nanoparticles for Rewritable Patterning and Dual-color Cell Imaging. Macromolecules 2015, 48, 3500–3508. (c) Dalal, C.; Jana, N. R. Riboflavin-terminated, Multivalent Quantum Dot as Fluorescent Cell Imaging Probe. Langmuir 2019, 35, 11380–11388.

(28) (a) Rana, S.; Elci, S. G.; Mout, R.; Singla, A. K.; Yazdani, M.; Bender, M.; Bajaj, A.; Saha, K.; Bunz, U. H. F.; Jirik, F. R.; Rotello, V. M. Ratiosymmetric Array of Conjugated Polymers—fluorescent Protein Provides a Robust Mammalian Cell Sensor. J. Am. Chem. Soc. 2016, 138, 4522–4529. (b) Liu, Z.; Chen, N.; Dong, C.; Li, W.; Guo, W.; Wang, H.; Wang, S.; Tan, J.; Tu, Y.; Chang, J. Facile Construction of Near Infrared Fluorescent Nanoprobe with Amphiphilic Protein-biocompatible Probe for Targeted Cell Imaging. ACS Appl. Mater. Interfaces 2015, 7, 18997–19005.

(29) (a) Dmitriev, R. I.; Borisov, S. M.; Diussmann, H.; Sun, S.; Müller, B. J.; Prehn, J.; Baklauchev, V. P.; Klimov, V. P.; Pavlovsky, D. B. Versatile Conjugated Polymer Nanoparticles for High-O3 Imaging in Cells and 3D Tissue Models. ACS Nano 2015, 9, 5275–5288. (b) Gonil, P.; Sajomangs, W.; Ruktanonchai, U. R.; Na Ubol, P.; Treetong, A.; Opanasopit, P.; Puttipipatkachorn, S. Synthesis and Fluorescence Properties of N-Substituted 1-
Cyanobenz[f]isoindole Chitosan Polymers and Nanoparticles for Live Cell Imaging. Biomacromolecules 2014, 15, 2879–2888. (c) Bajj, D. N. F.; Tran, M. V.; Tsai, H.-Y.; Kim, H.; Paisley, N. R.; Algar, W. R.; Hudson, Z. M. Fluorescent Heterotelechelic Single-chain Polymer Nanoparticles: Synthesis, Spectroscopy, and Cellular Imaging. ACS Appl. Nano Mater. 2019, 2, 898–909. (30) (a) Roy, D.; Sumerlin, B. S. Glucose-sensitivity of Boronic Acid Block Copolymers at Physiological pH. ACS Macro Lett. 2012, 1, 529–532. (b) Chua, G. B. H.; Roth, P. J.; Duong, H. T. T.; Davis, T. P.; Lowe, A. B. Synthesis and Thermoresponsive Solution Properties of Poly(oligo(ethylene glycol) (meth)acrylamide)s: Biocompatible PEG Analogues. Macromolecules 2012, 45, 1362–1374. (31) (a) Ru, Y.; Zhang, X.; Song, W.; Liu, Z.; Feng, H.; Wang, B.; Guo, M.; Wang, X.; Luo, C.; Yang, W.; Li, Y.; Qiao, J. A New Family of Thermoplastic Photoluminescence Polymers. Polym. Chem. 2016, 7, 6250–6256. (b) Zhao, E.; Lam, J. W. Y.; Meng, L.; Hong, Y.; Deng, H.; Bai, G.; Huang, X.; Hao, J.; Tang, B. Z. Poly[maleic anhydride]-alt-(vinyl acetate): A Novel Oxygenic Nonconjugated Macromolecule with Strong Light Emission and Solvatochromic Effect. Macromolecules 2015, 48, 64–71. (c) Han, T.; Deng, H.; Qiu, Z.; Zhao, Z.; Zhang, H.; Zou, H.; Leung, N. L. C.; Shan, G.; Elsegood, M. R. J.; Lam, J. W. Y.; Tang, B. Z. Facile Multicomponent Polymerizations toward Unconventional Luminescent Polymers with Readily Openable Small Heterocycles. J. Am. Chem. Soc. 2018, 140, 5588–5598. (d) Yan, J.-J.; Wang, Z.-K.; Lin, X.-S.; Hong, C.-Y.; Liang, H.-J.; Pan, C.-Y.; You, Y.-Z. Polymerizing Nonfluorescent Monomers without Incorporating any Fluorescent Agent Produces Strong Fluorescent Polymers. Adv. Mater. 2012, 24, 5617–5624. (32) Chen, R.; Tang, Y.; Wan, Y.; Chen, T.; Zheng, C.; Qi, Y.; Cheng, Y.; Huang, W. Promoting Singlet/triplet Exciton Transformation in Organic Optoelectronic Molecules: Role of Excited State Transition Configuration. Sci. Rep. 2017, 7, 6225. (33) Bauri, K.; Saha, B.; Mahanti, J.; De, P. A Nonconjugated Macro-molecular Luminogen for Speedy, Selective and Sensitive Detection of Picric Acid in Water. Polym. Chem. 2017, 8, 7180–7187. (34) Li, Y.; Liu, K.; Li, W.-J.; Guo, A.; Zhao, F.-Y.; Liu, H.; Ruan, W.-J. Coordination Polymer Nanoarchitecture for Nitroaromatic Sensing by Static Quenching Mechanism. J. Phys. Chem. C 2015, 119, 28544–28550. (35) (a) Luo, C.; Liu, Y.; Zhang, Q.; Cai, X. Hyperbranched Conjugated Polymers Containing 1,3-Butadiene Units: Metal-free Catalyzed Synthesis and Selective Chemosensors for Fe3+ Ions. RSC Adv. 2017, 7, 12269. (b) Hou, B.-L.; Tian, D.; Liu, J.; Dong, L.-Z.; Li, S.-L.; Li, D.-S.; Lan, Y.-Q. A Water-stable Metal–organic Framework for Highly Sensitive and Selective Sensing of Fe3+ Ion. Inorg. Chem. 2016, 55, 10580. (c) Ma, T.; Zhao, X.; Matsu, Y.; Song, J.; Zhao, R.; Faheem, M.; Chen, M.; Zhang, Y.; Tian, Y.; Zhu, G. Fluorescent-based Fluorescent Porous Aromatic Framework for Fe3+ Detection with High Sensitivity. J. Mater. Chem. C 2019, 7, 2327. (36) (a) Singha, N. R.; Mahapatra, M.; Karmakar, M.; Mondal, H.; Dutta, A.; Deb, M.; Mitra, M.; Roy, C.; Chattopadhyay, P. K.; Maiti, D. K. In Situ Allocation of a Monomer in Pectin-g-Terpolymer Hydrogels and Effect of Comonomer Compositions on Superadsorption of Metal Ions/Dyes. ACS Omega 2018, 3, 4163–4180. (b) Mondal, H.; Karmakar, M.; Dutta, A.; Mahapatra, M.; Deb, M.; Mitra, M.; Roy, J. S. D.; Roy, C.; Chattopadhyay, P. K.; Singha, N. R. Tetrapolymer Network Hydrogels via Gumghatti Grafted and N-H/C–H Activated Allocation of Monomers for Composition Dependent Superadsorption of Metal Ions. ACS Omega 2018, 3, 10692–10708. (37) (a) Singha, N. R.; Karmakar, M.; Mahapatra, M.; Mondal, H.; Dutta, A.; Roy, C.; Chattopadhyay, P. K. Systematic Synthesis of Pectin-g-(sodium acrylate-co-N-isopropylacrylamide) Interpenetrating Polymer Network for Superadsorption of Dyes/M(II): Determination of Physicochemical Changes in Loaded Hydrogels. Polym. Chem. 2017, 8, 3211–3237. (b) Singha, N. R.; Roy, C.; Mahapatra, M.; Dutta, A.; Deb, Roy, J. S.; Mitra, M.; Chattopadhyay, P. K. Scalable Synthesis of Collagenic-Waste and Natural Rubber-Based Biocomposite for Removal of Hg(II) and Dyes: Approach for Cost-Friendly Waste Management. ACS Omega 2019, 4, 421–436. (38) Sillen, A.; Engelborghs, Y. The Correct Use of “Average” Fluorescence Parameters. Photochem. Photobiol. 1998, 67, 475–486.