Visualizing molecular weights differences in supramolecular polymers

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Issues of molecular weight determination have been central to the development of supramolecular polymer chemistry. Whereas relationships between concentration and optical features are established for well-behaved absorptive and emissive species, for most supramolecular polymeric systems no simple correlation exists between optical performance and number-average molecular weight (Mn). As such, the Mn of supramolecular polymers have to be inferred from various measurements. Herein, we report an anion-responsive supramolecular polymer [M1 Zn(OTf)2]n, that exhibits monotonic changes in the fluorescence color as a function of Mn. Based on theoretical estimates, the calculated average degree of polymerization (DPav) increases from 16.9 to 84.5 as the monomer concentration increases from 0.08 mM to 2.00 mM. Meanwhile, the fluorescent colors of M1 + Zn(OTf)2 solutions were found to pass from green to yellow and to orange, corresponding to a red shift in the maximum emission band (λmax). Therefore, a relationship between DPav and λmax could be established. Additionally, the anion-responsive nature of the present system meant that the extent of supramolecular polymerization could be regulated by introducing anions, with the resulting change in Mn being readily monitored via changes in the fluorescent emission features.

supramolecular polymers | molecular weight | fluorescence | J-aggregate | self-assembly

Molecular weight determinations play a vital role in the characterization of supramolecular polymers. They are essential to assessing the degree of polymerization, which can have a significant impact on the properties of the polymer. While various characterization methods have been developed to estimate the number-average molecular weight (Mn) of supramolecular polymers, a simple visual method could provide advantages in terms of ease of use. We have now developed a system wherein differences in the fluorescent signature, including changes in color, allow variations in the Mn of an anion-responsive supramolecular polymer [M1 Zn(OTf)2]n, to be readily monitored. The present visual differentiation strategy provides a tool that may be used to characterize supramolecular polymers.

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(Raoult’s law), can be used to deduce the molar mass of supramolecular polymers (50, 51). Matrix-assisted laser desorption ionization time-of-flight mass spectrometry has also been exploited to characterize oligomers and various relatively small self-assembled ensembles (52, 53). The molecular weights ($M_n$) of supramolecular polymers can also be inferred from concentration-dependent chemical shift changes in the corresponding $^1$H NMR spectra (54). Separately, single-molecule force spectroscopy experiments have been used to determine the length of the bridges between the tip and substrate formed by supramolecular polymers, thus providing insights into the effective molecular weight of the polymer (55). These techniques notwithstanding, there remains a need for simple methods that would allow changes in the molecular weight of supramolecular polymers to be determined by optical means. Here, we report a system where a simple correlation is established between the fluorescence emission features and the $M_n$ of a supramolecular polymer.

The present approach is based on an appreciation that $J$-type dyes have been identified in a variety of aggregation modes (56–59), including monomer, dimer, and stacked arrangements. Dyes of this type, which include a number of polycyclic and heterocyclic aromatic molecules, typically display fluorescent colors that vary as a function of concentration. Therefore, we postulated that incorporating $J$-type dyes into appropriately chosen monomers would endow the resulting putative supramolecular polymers with variable fluorescent colors, the specifics of which could be correlated with the degree of polymerization (Fig. 1).

With such thinking in mind, we synthesized monomer $M_1$ by modifying a $J$-type dye, naphthalene diimide (NDI) (60, 61), with two alkylated terpyridine derivatives at both ends (Fig. 1). The NDI-derived $M_1$ interacts with Zn(OTf)$_2$ in DMF/H$_2$O (1/4, vol/vol) solution through terpyridine–Zn$^{2+}$ coordination. At low monomer concentrations, these two components were expected to self-assemble into cyclic species or short oligomers characterized by long distances between the NDI subunits. Thus, little stacking would be seen, resulting in a green, monomer-dominated fluorescence for dilute $M_1$ + Zn(OTf)$_2$ solutions. As the total monomer concentration is increased with the ratio of $M_1$ and Zn(OTf)$_2$, the cyclic species would be expected to transform gradually into linear supramolecular polymers, [M$_1$-Zn(OTf)$_2$]$_n$. Under these conditions, a limited degree of interchain association (e.g., the formation of double-strand dimers) is expected, leading to a decrease in the distance between NDI groups and a change in the fluorescent color from green to yellow. Upon increasing the monomer concentration, a corresponding increase in the polymer chain length is expected, which will lead to tight entanglement between individual polymer chains, further reducing the average distance between the emissive NDI groups. In the limit, this reduction in inter-NDI spacing would lead to formation of $J$-aggregates, which in the case of the NDI-containing $M_1$ component would give rise to orange-colored fluorescence. In accord with prior work involving supramolecular polymers (27, 38), we also appreciated that anion recognition could be used to adjust the molecular weight of the supramolecular polymers formed from $M_1$ and Zn(OTf)$_2$. Specifically, we expected that adding tetraethylammonium hydroxide (TBAOH) to [M$_1$-Zn(OTf)$_2$]$_n$ would lead to depolymerization as the result of complexion between the OH$^-$ anions and Zn$^{2+}$. This would lead to restoration of the initial emission color. As detailed below, these design expectations were realized. Specifically, the $M_n$ of the supramolecular aggregates formed from $M_1$ and Zn(OTf)$_2$ produced in dimethylformamide (DMF)/H$_2$O (1/4, vol/vol) solution could be distinguished by monitoring the fluorescent colors as a function of $M_1$ + Zn(OTf)$_2$ and TBAOH concentration.

**Results and Discussion**

**Synthesis of $M_1$ and Preparation of $M_1$ + Zn(OTf)$_2$ Solutions.** The synthetic procedure used to access monomer $M_1$ is shown in SI Appendix, Fig. S1. $M_1$ and its precursors were characterized by means of $^1$H NMR spectroscopy, $^1$C NMR spectroscopy, and high-resolution mass spectrometry (SI Appendix, Figs. S2–S13). To prepare $M_1$ + Zn(OTf)$_2$ solutions (SI Appendix, Fig. S14), equimolar solutions of monomer $M_1$ and Zn(OTf)$_2$ were made up in chloroform (1.25 mL) and methanol (1.25 mL), respectively. These two solutions were then combined and stirred for 1 h at 298 K. The resulting mixture was subject to slow evaporation at 298 K giving $M_1$-Zn(OTf)$_2$ as a solid, which subsequently was dissolved in DMF/H$_2$O (1/4, vol/vol) to give a stock solution of $M_1$ + Zn(OTf)$_2$ (2.00 mM, 500 μL). Standard solutions of $M_1$ + Zn(OTf)$_2$ (0.08 to 1.80 mM) were then prepared by diluting this $M_1$ + Zn(OTf)$_2$ stock solution (2.00 mM) with DMF/H$_2$O (1/4, vol/vol). Note that the concentrations of $M_1$ + Zn(OTf)$_2$ mentioned in this article refer to the total monomer concentration [i.e., the sum of the $M_1$ + Zn(OTf)$_2$ concentrations]. Unless otherwise noted, the ratio of $M_1$ and Zn(OTf)$_2$ was held constant at 1:1.

**Job Plots and Ultraviolet-Visible Spectroscopic Titrations.** To obtain insights into the interactions between $M_1$ and Zn(OTf)$_2$, the complexation between precursor 1a (Fig. 2A) and Zn(OTf)$_2$ was studied using the Job method (62–64). As shown in Fig. 2A, an adsorption peak for 1a in DMF/H$_2$O (1/4, vol/vol) was observed at 285 nm, whose intensity decreased as the molar ratio of [Zn(OTf)$_2$]/([Zn(OTf)$_2$] + [1a]) increased. An absorbance feature at 340 nm was also seen that increased in intensity initially but then declined as the molar ratio of [Zn(OTf)$_2$]/([Zn(OTf)$_2$] + [1a]) increased. The changes in the absorbance at 340 nm were plotted against the molar ratio of [Zn(OTf)$_2$]/([Zn(OTf)$_2$] + [1a]) to give a Job’s plot (Fig. 2B) (63). This plot revealed an absorbance maximum when the molar fraction of [Zn(OTf)$_2$]$_2$ was 0.33. While not a proof, this finding is consistent with a 1:2 binding stoichiometry in this solvent system, wherein each Zn$^{2+}$ ion complexes two molecules of 1a.

The binding between compound 1a and Zn(OTf)$_2$ was further studied by means ultraviolet-visible (UV-vis) spectroscopic titrations (Fig. 2C) (65). Upon the addition of Zn(OTf)$_2$ to a dilute solution of 1a in DMF/H$_2$O (1/4, vol/vol), a decline in the original adsorption peak at 285 nm is seen. Concurrently, a new peak at 340 nm is seen to grow in. This latter spectral feature is attributed to the formation of octahedral complexes characterized by distinct metal–ligand charge transfer bands (66). Titration curves were constructed by plotting...
the absorbance at 340 nm and the Zn(OTf)₂ concentration (0.00 to 1.00 equiv.) could be reproduced no appreciable changes in the absorbance intensity at 340 nm. The relationship between the absorbance at 340 nm and the Zn(OTf)₂ concentration was then constructed (Fig. 2D). The degree of polymerization calculated (DPcal) for equimolar mixtures of M1 and Zn(OTf)₂ (0.08 to 2.00 mM).

**Visualizing Method.** To provide evidence that a supramolecular polymer, [M1-Zn(OTf)₂]₀, was formed from a mixture of M1 and Zn(OTf)₂, we determined the specific viscosity of various M1+Zn(OTf)₂ solutions (0.08 to 2.00 mM) (70, 71). A double logarithmic plot of the specific viscosity versus the total concentration of these two monomers increased from 0.08 to 0.20 mM, the specific viscosity rose steadily with a slope of 0.256. When the total concentration of M1+Zn(OTf)₂ was increased past 0.40 mM, there was a dramatic increase in the specific viscosity, with a slope of 1.14 being seen. The concentration of M1+Zn(OTf)₂ corresponding to the intersection of two fitted linear lines (0.22 mM) was defined as the CPC (70). The slope in the low concentration range reflects the characteristics of cyclic species or oligomers expected in dilute solutions. Conversely, the dramatic increase in the specific viscosity seen above the CPC is ascribed to the formation of linear supramolecular polymers and the entanglement between individual linear polymers. Therefore, these results support the design expectation that supramolecular polymers would form at high total monomer concentrations, while relatively small oligomers would form at lower monomer concentrations.

**Scanning Electron Microscopic, Atomic Force Microscopic, and Laser Scanning Confocal Microscopic Studies of Equimolar Mixtures of M1 and Zn(OTf)₂.** Additional evidence for the formation of supramolecular polymers of generalized structure [M1-Zn(OTf)₂]₀ came from morphology experiments (72). Scanning electron microscopic (SEM) images of M1+Zn(OTf)₂ determined at different concentrations of M1+Zn(OTf)₂ are shown in Fig. 3A. At total concentrations below 0.20 mM, only particle-like structures are...
observed. However, fibrous structures (73) are seen when the total concentration reached 0.20 mM. The length of these fibers was seen to grow as the monomer concentration was increased further from 0.20 mM to 2.00 mM, as would be expected given the proposed formation of $[\text{M1}/\text{C1}]\text{Zn(OTf)2}]_n$.

Atomic force microscopy (AFM) is another powerful tool that may be used to determine the morphology of self-assembled materials (74). Thus, $[\text{M1}/\text{C1}]\text{Zn(OTf)2}]_n$ was analyzed at different monomer concentrations via tapping-mode AFM (75). Consistent with the images captured through SEM, micro-sized particles were observed by AFM over the 0.08 mM to 0.16 mM monomer concentration regime, while fibrous species of increasing size were seen as the monomer concentration was increased past 0.20 mM; this was accompanied by a decrease in the number of visible particles (Fig. 3B). Again, these findings thus provided an initial indication that a useful relationship might exist between the monomer concentration and the fluorescence features of the self-assembled species formed from 1:1 mixtures of M1 and Zn(OTf)2.

Fluorescence Properties of Equimolar Mixtures of M1 and Zn(OTf)2. To test the presumed relationship between monomer concentration and the fluorescence emission in our system, we monitored the colors of 1:1 $\text{M1} + \text{Zn(OTf)2}$ solutions in DMF/H2O (1/4, vol/vol) at different total monomer concentrations under UV excitation. As shown in Fig. 3D and Movie S1, as the monomer concentration increased different colors were observed. In accord with the LSCM study above, the colors evolved from green to yellow and then to orange with increasing $\text{M1} + \text{Zn(OTf)2}$ concentration.

Fluorescence colors shown for the LSCM images (Fig. 3C) were then generated using the fluorescence colors of $\text{M1} + \text{Zn(OTf)2}$ solutions under UV excitation (hand-held lamp; 365 nm) (Fig. 3D). As shown in Fig. 3C, micrrosized particles were observed at a total monomer concentration of 0.08 mM. As the monomer concentration increased, fibrous species first appeared and then increased in size. A concurrent change in the color of the samples was also observed, revealing distinct differences in the fluorescence properties as a function of the dynamic assembly process. Notably, as the monomer concentration was raised from 0.08 mM to 0.16 mM, the fluorescent color of the samples evolved, changing from dark green to green. When the total monomer concentration reached 0.40 mM (corresponding to formation of a fibrous structure) a yellow fluorescence was seen. An orange fluorescence was seen at $\text{M1} + \text{Zn(OTf)2}$ concentrations over 0.40 mM. These findings thus provided an initial indication that a useful relationship might exist between the monomer concentration and the fluorescence features of the self-assembled species formed from 1:1 mixtures of M1 and Zn(OTf)2.

Fig. 3E shows in cartoon fashion our proposed mechanistic rationale for the observed fluorescent color changes. At low total monomer concentrations (0.08 to 0.20 mM), $\text{M1}$ and Zn(OTf)2 self-assemble to form cyclic species or oligomers. Under these conditions, the probability of contact between $\text{M1}$ subunits is low, resulting in a large separation between the emissive NDI groups. Thus, a monomer-like green NDI-based...
emission is seen. As the total monomer concentration approaches the CPC (0.22 mM), supramolecular polymers start to form, contributing to more chain-to-chain contacts. These contacts serve to reduce the distance between the NDI groups, prompting a change in the fluorescent color from green to yellow. A further increase in the monomer concentration (0.60 to 2.00 mM) leads to an increase in the polymer size and molecular weight and interchain entanglement; this further shortens the distance between the NDI groups and supports formation of J-aggregates characterized by an orange emission.

To quantify the relationship between color and monomer concentration the emission spectra of 1:1 solutions of M1 and Zn(OTf)₂ were recorded as a function of total monomer concentration. Note that an excitation wavelength of 410 nm was employed. The normalized emission spectra (475 to 725 nm) for these M1 + Zn(OTf)₂ solutions over the 0.08 mM to 2.00 mM concentration range are shown in Fig. 4A. The corresponding emission maxima (λ_{max}) are shown in Fig. 4B. When the monomer concentration is increased from 0.08 mM to 0.20 mM, a shift of only 4 nm in λ_{max} from 481 nm to 485 nm is seen. This finding is consistent with the monomeric form of NDI dominating within this concentration regime. However, as the concentration reached 0.40 mM, a remarkable redshift in the λ_{max} to 532 nm was observed, a finding interpreted in terms of the formation of substantial quantity of the dimeric NDI form. At high concentrations (i.e., >0.60 mM), the λ_{max} shifts steadily from 534 nm to 560 nm as a function of concentration. This finding is interpreted in terms of larger-sized π-stacked structures dominating in this concentration regime. These results led us to infer that a dependent relationship between the monomer concentration and the observed λ_{max} pertains for solutions of M1 + Zn(OTf)₂ (58, 79). Additionally, the emission spectra of these M1 + Zn(OTf)₂ solutions were recorded over the 0.08 mM to 2.00 mM range and used to generate a Commission Internationale de l’Eclairage (CIE) diagram (SI Appendix, Fig. S23). This CIE diagram proved concordant with the colors shown in Fig. 3D (80).

**Relationship between DP**_**cal** and the Maximum Emission Wavelength.** The inferred dependent relationship between 1) the total monomer concentration and the DP_{cal} (Fig. 2E) and 2) between the monomer concentration and the observed λ_{max} (Fig. 4B) allowed us to correlate the λ_{max} with DP_{cal} as shown in Fig. 5. As the DP_{cal} increases from 16.9 to 26.7 only a slight shift in λ_{max} from 481 nm to 485 nm is seen. In contrast, a dramatic shift in λ_{max} to 532 nm, corresponding to a DP_{cal} of 37.8, was observed (Fig. 5A). A further remarkable shift in λ_{max} from 534 nm to 560 nm occurred as the DP_{cal} rose from 46.3 to 53.4. As the DP_{cal} was then increased to 84.5, a steady increase in the λ_{max} (from 560 nm to 566 nm) was seen (Fig. 5B). Additionally, the DP_{cal} of the supramolecular polymer [M1·Zn(OTf)₂]ₙ could be visually distinguished due to changes in the color of the solutions (Fig. 5B). Over the DP_{cal} range of 16.9 to 26.7, the fluorescent color of the solutions changed slightly from dark green to green. Then, as the DP_{cal} climbed to 37.8, a yellow fluorescence emission was observed, which changed to orange at a DP_{cal} of 46.3, a color that deepened as the DP_{cal} further increased to 84.5.

**Preparation of Monomer M1 Solutions.** Given that interactions between M1 monomers that are independent of supramolecular polymer formation may contribute to the observed fluorescence behavior, the above tests were repeated for pure M1 solutions under otherwise identical conditions. As above, an M1 stock solution (1.00 mM) was prepared by dissolving M1 in DMF/H₂O (1/4, vol/vol). Standard solutions of M1 (0.04 to 0.90 mM) were then obtained by diluting this stock solution.

**Viscosity Studies.** The aggregation of M1 was studied initially via viscosity tests. A double logarithmic plot of specific viscosity versus DP_{cal} concentration is shown in SI Appendix, Fig. S22. In contrast to what was seen in the case of the corresponding M1 + Zn(OTf)₂ solutions no pronounced changes in the slope were observed as a function of concentration; rather, the specific viscosities increased slowly over the full M1 concentration range, with a slope of 0.151. Of note is that the slope (0.151) in the M1 diagram is relatively close to the slope (0.256) recorded for M1 + Zn(OTf)₂ solutions at relatively low concentration (0.04 to 0.20 mM). On this basis, we infer that only small-sized assemblies or nonsupramolecular polymer aggregates are formed from M1 in DMF/H₂O (1/4, vol/vol) (64).

**SEM, AFM, and LSCM Studies of M1.** To explore further the aggregation modes of M1 in DMF/H₂O (1/4, vol/vol), solutions of M1 were subject to SEM, AFM, and LSCM analysis. In the SEM images (Fig. 6A), tiny particles were seen over the 0.04 mM to 0.10 mM M1 concentration range. The size of these particles was seen to grow gradually as the concentration increased to 1.00 mM; however, no fibrous species were observed. This leads us to suggest that M1 alone does not support the formation of supramolecular polymers. Consistent with this inference, only microsized particles were captured via AFM (Fig. 6B). The resulting LSCM outputs were treated as above to give
colored images (Fig. 6D). These analyses revealed (Fig. 6C) that the number and size of the particles increased gradually with increasing M1 concentration; however, no evidence of supramolecular polymer formation was seen. At low concentrations these particles were green in color and became yellow-green color at higher concentrations as seen in the LSCM images. Specifically, no further obvious color transitions were seen in contrast to what was observed for the M1 + Zn(OTf)2 solutions.

**Fluorescence Properties of Monomer M1.** The fluorescent colors of M1 solutions at various concentrations were also recorded under UV light. As shown in Fig. 6D and Movie S2, as the M1 concentration was increased from 0.04 mM to 0.10 mM and then to 0.20 mM, the fluorescent color evolved from dark green to green to yellow-green. We thus conclude that at higher concentrations the monomeric form of M1 exists in equilibrium with stacked dimeric structures as illustrated in Fig. 6E. As the relative concentration of dimers increases, the fluorescence color becomes increasing yellow-green. No evidence of the highly aggregated orange emissive form is seen.

The normalized fluorescence spectra of the M1 solutions were also recorded at various concentrations. As shown in Fig. 7, an increase in the M1 concentration from 0.04 mM to 1.00 mM leads to a shift in the M1 emission maximum from 481 nm to 525 nm. This net 44 nm shift in the $\lambda_{\text{max}}$ is significantly lower than the difference in $\lambda_{\text{max}}$ (85 nm) seen for equimolar solutions of M1 + Zn(OTf)2 as the concentration is similarly increased. Additionally, a yellow-green fluorescence is seen for 0.50 mM to 1.00 mM solutions of M1; in contrast, corresponding solutions of M1 + Zn(OTf)2 are characterized by an orange fluorescence emission. Taken in concert, these results provide support for the suggestion that supramolecular polymerization occurs in the case of M1 + Zn(OTf)2 in DMF/H2O (1/4, vol/vol), but not for solutions of M1 alone.

**Fig. 6.** Morphology, fluorescence behavior, and origin of the M1-derived fluorescence. (A) SEM images, (B) AFM images, and (C) LSCM images of M1 solutions at different concentrations (0.04, 0.08, 0.10, 0.20, 0.40, 0.60, and 1.00 mM in DMF/H2O [1/4, vol/vol]). $\lambda_{\text{ex}} = 405$ nm. (D) Photographs of M1 solutions (0.04 to 1.00 mM) recorded using a hand-held UV lamp. (E) Cartoon representations showing the various limiting self-assembled form of M1 and the fluorescence color changes expected as the concentration of the monomers is increased. (Scale bars: A, 100 μm; B, 20.0 μm; C, 100 μm.)

**Fig. 7.** Fluorescence characterization of M1. Normalized fluorescent spectra of solutions of M1 recorded from 0.04 to 1.00 mM in DMF/H2O (1/4, vol/vol) at 298 K. $\lambda_{\text{ex}} = 410$ nm. Slit: 10/15.
Anion Responsiveness of \([\text{M1-Zn(OTf)}_2]_n\). We next sought to test whether the supramolecular polymer \([\text{M1-Zn(OTf)}_2]_n\) would display anion-responsive disaggregation behavior. Since the distinctive fluorescent properties of \([\text{M1-Zn(OTf)}_2]_n\), were attributed to stacked structures involving the NDI groups, it was expected that anion-induced depolymerization, to the extent it occurred, would be reflected in a readily discernible change in the fluorescent properties of the system. To test this proposition, TBAOH was added to preformed solutions \([\text{M1-Zn(OTf)}_2]_n\). According to previous reports, the \(\text{OH}^-\) anion was expected to interact strongly with the \(\text{Zn}^{2+}\) cation to form \(\text{Zn(OH)}_2\) (Fig. 8A), thus breaking up the chelate complexes that provides the stabilization for the supramolecular polymer \([\text{M1-Zn(OTf)}_2]_n\). Upon addition of 20.0 equiv. of \(\text{OH}^-\) to a 2.00 mM solution of \(\text{M1-Zn(OTf)}_2\), only granular species were seen by SEM (Fig. 8B) and AFM (Fig. 8C). Additionally, only green particles were observed in the corresponding LSCM images (Fig. 8D), rather than the orange fibrous species seen for \([\text{M1-Zn(OTf)}_2]_n\) in the absence of TBAOH. Moreover, after adding \(\text{OH}^-\) (20.0 equiv.) to a 2.00 mM solution of \(\text{M1-Zn(OTf)}_2\) and removing the precipitate that formed (presumed to be zinc hydroxide), the color of the fluorescent solution changed from orange to green when irradiated with a handheld UV lamp. Finally, as shown in Fig. 8E, incorporation of TBAOH also provoked a blue shift in the \(\lambda_{\text{max}}\) from 566 nm to 485 nm. On the basis of these combined results we conclude that the \(\text{OH}^-\) anion acts as a stimulus that depolymerizes \([\text{M1-Zn(OTf)}_2]_n\), thereby inducing a readily discernible change in the fluorescent color. This change in color can, in turn, be used to monitor the breakup of the \(J\)-aggregates present in the initial supramolecular polymer.

**Conclusion**

In conclusion, we present here two supramolecular monomers, a terpyridine modified NDI (M1) and Zn(OTf)_2, which can self-assemble into aggregated species driven by the coordination between terpyridine and Zn(OTf)_2. The formation of an anion-responsive supramolecular polymer, \([\text{M1-Zn(OTf)}_2]_n\), at higher concentrations was inferred on the basis of UV-vis spectroscopic titrations, as well as viscosity, SEM, AFM, and LSCM studies. Based on theoretical estimates, an increase in monomer concentration from 0.08 mM to 2.00 mM was expected to lead to an increase in the \(D_{\text{Pcal}}\) from 16.9 to 84.5. Over this concentration range, a change in the fluorescent colors from green to yellow to orange, corresponding to a shift in \(\lambda_{\text{max}}\) from 481 nm to 566 nm, was observed by experiment. A dependent relationship between \(D_{\text{Pcal}}\) and \(\lambda_{\text{max}}\) was established by combining the data for monomer concentration, \(D_{\text{Pcal}}\) and \(\lambda_{\text{max}}\). As the \(D_{\text{Pcal}}\) increased from 16.9 to 37.8 and then to 84.5, the \(\lambda_{\text{max}}\) of \(\text{M1-Zn(OTf)}_2\) (as a DMF/H_2O (1/4, vol/vol) solution) shifted from 481 (green) to 532 (yellow) and then to 566 nm (orange). These spectral shifts were rationalized in terms of the supramolecular assembly-induced aggregation of NDI groups. With increasing monomer concentration, cyclic species/oligomers were firstly transformed to supramolecular polymers, and then to more fully entangled polymer-containing ensembles. These self-assembly processes, in turn, lead to a reduction in the distance between individual NDI groups, as \(\text{M1}\)-containing monomers are converted to dimeric forms and then to \(J\)-aggregated forms. Conversely, the specific addition of a hydroxide anion source to preformed \([\text{M1-Zn(OTf)}_2]_n\) was found to induce depolymerization and to restore the original fluorescence signature. Finally, the combination of different colors and fluorescence spectral features allowed changes in the \(D_{\text{Pcal}}\) and corresponding differences in the supramolecular polymer molecular weights to be distinguished visually. The present optical-based differentiation strategy is expected to be generalizable and may prove useful in the characterization of supramolecular polymers containing appropriately chosen fluorophores.

**Materials and Methods**

Full experimental details and procedures for the synthesis of the compounds used in the present study, molecular structures, viscosity studies of \(\text{M1-Zn(OTf)}_2\) solutions and \(\text{M1}\) solutions, preparation of \(\text{M1-Zn(OTf)}_2\) solutions.
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