Polymer glasses have an irregular structure. Among the causes for such complexity are the chemically distinct chain end-groups that are the most abundant irregularities in any linear polymer. In this work we demonstrate that chain end induced defects allow polymer glasses to create confined environments capable of hosting small emissive molecules. Using environmentally sensitive luminescent complexes we show that the size of these confinements depends on molecular weight and can dramatically affect the photoluminescence of free or covalently bound emissive complexes. We confirm the impact of chain end confinement on the bulk glass transition in poly(methyl acrylate) and show that commonly observed $T_g$ changes induced by the chain ends should have a structural origin. Finally, we demonstrate that size and placement of luminescent molecular probes in pMA can dramatically affect the probe luminescence and its temperature dependence suggesting that polymer glass is a highly irregular and complex environment marking its difference with conventional small molecule solvents. Considering the ubiquity of luminescent glassy materials, our work lays down a blueprint for designing them with structural considerations in mind, ones where packing density and chain end size are key factors.
Environmentally Sensitive Luminescence Reveals Spatial Confine-
ment, Dynamics and Their Molecular Weight Dependence in a Poly-
mer Glass

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KEYWORDS: luminescence, confinement, responsive polymers, glass transition, copper

ABSTRACT: Polymer glasses have an irregular structure. Among the causes for such complexity are the chemically distinct chain end-groups that are the most abundant irregularities in any linear polymer. In this work we demonstrate that chain end induced defects allow polymer glasses to create confined environments capable of hosting small emissive molecules. Using environmentally sensitive luminescent complexes we show that the size of these confinements depends on molecular weight and can dramatically affect the photoluminescence of free or covalently bound emissive complexes. We confirm the impact of chain end confinement on the bulk glass transition in poly(methyl acrylate) and show that commonly observed $T_g$ changes induced by the chain ends should have a structural origin. Finally, we demonstrate that size and placement of luminescent molecular probes in pMA can dramatically affect the probe luminescence and its temperature dependence suggesting that polymer glass is a highly irregular and complex environment marking its difference with conventional small molecule solvents. Considering the ubiquity of luminescent glassy materials, our work lays down a blueprint for designing them with structural considerations in mind, ones where packing density and chain end size are key factors.

Introduction

Polymers are highly complex materials from a structural and a dynamic point of view. A local, molecular level characterization of such complexity in polymers and soft matter can be achieved using small molecule probes that can be placed within materials and provide information about its surroundings. Several approaches to probe-based techniques gained traction in the last decades. Historically, one of the first practices in the field employed probes for fluorescence spectroscopy correlation studies. Using these fluorophores it was possible to track molecular mobility and dynamic heterogeneity in polymer glasses and characterize chain dynamics and local viscosity. Stable luminescence is one of the main requirement for correlation spectroscopy probes that are otherwise environmentally insensitive, i.e. their luminescence varies marginally when the polymer environment changes.

Alternative characterization approach utilizes molecular probes with environmentally sensitive luminescence. Such probe molecules can, for example, vary their emission color or intensity in response to changes of polymer aggregation state, viscosity and free volume characteristics. While these probes can be more chemically complex, they often provide a simple color or intensity based response that is easy to detect and analyze. Perhaps the most illustrative of the practice is the recent report by Christie, Register and Priestley who used a simple pyrene dye to perform local $T_g$ analysis in block copolymers. These authors demonstrated that local $T_g$ can vary significantly, by tens of degrees, in lamellar PMMA/PBMA block copolymers within the space of several nanometers.

The latter work demonstrates the importance of probe placement chemistry for interpreting the photoluminescence (PL) data. Since different parts of material can exhibit different extent dynamics, even a common choice between tethered or freely dispersed probes defines which space in the polymer will be accessible to the probe molecules and which aspect of polymer dynamics they will ultimately describe. This touches on the principal questions one should ask when using responsive small molecules: How informative are local probe-based measurements and which local and bulk material features do they report?

In this work we demonstrate that by controlling the structure and placement of molecular probes one can distinguish between their local and global mode of operation. This approach reveals pronounced differences in glass transition behavior of the polymer bulk and the chain end groups and connects the latter to the free volume characteristics of the parent polymer that are shown to be molecular weight dependent. Importantly, we show how minor variations, benign from a synthetic chemistry standpoint, have a dramatic impact on the probe luminescence.
We point out that such variations in luminescence color have structural origin, carry information about the environment surrounding the emissive complexes and can generally occur in any polymer glass blended with emissive molecules.

As the majority of molecular probes are several dozens of atoms in size, we center this work around a similarly sized irregularity found in any linear polymer – the polymer chain end groups. While being a small fraction of the polymer, the chemical structure of the end groups is known to impact the bulk Tg. An example of this behavior has recently been demonstrated by Torkelson and coworkers20 who reported Tg perturbations of nearly 35K for polystyrene samples of Mw ~ 4kDa with chemically distinct end groups. Conceptually, end groups can be viewed as packing defects in a polymer melt or glass, having, as a consequence, higher available free volume compared to the rest of the chain.21 The contribution of chain ends and their number or concentration per unit volume is central to explaining the molecular weight (Mw) dependence of polymer properties, e.g. viscosity or glass transition temperature. A well-known model that illustrates this was postulated by Flory and Fox.22-23 In practice, it suggests that polymers with lower molecular weight and thus high chain end concentration typically have a lower Tg that saturates to an asymptotic value as Mw increases. Interestingly, in cyclic polymers having no chain ends the Tg(Mw) dependence is largely suppressed14-26 and low Mw cyclic polystyrenes27-28 are barely distinguishable by their Tg from cyclic PS of higher molecular weights.

These data highlights connection between the local polymer structure at the chain end groups and the glassy behavior of the bulk. Furthermore, the chain ends appears to be central to the establishment of Mw dependence of the polymer properties noted above. Assuming this phenomenon to have a structural origin we set out to test the capacity of molecular probes for studying the microscopic structure of glasses with the ultimate goal of connecting microscopic features with the bulk behavior.

Results and Discussion

In this work, we utilized a family of thermochromic phosphorescent probes recently developed by our group for ratiometric color-based bulk Tg characterization.29 Unlike the majority of emissive probes used, for example, in the fluorescent correlation spectroscopy studies3-10 the CuN4 probes (Figure 1) used in this work are designed to probe the material dynamics on the timescale of the probe photoluminescence (PL). Namely, the PL spectrum of CuN4 and its emission color is linked to the ion pair geometry within the probe molecule.30 Photoexcitation of CuN4 triggers a structural rearrangement of this ion pair which is strongly dependent on the mobility of the polymer hosting the probe (Figure 2). In the case of immobile ion pairs, like the ones found in a polymer glass, the ion pair distance is largely controlled by the local glass structure and its thermal expansion. In a polymer melt the ion pair is mobile and can rearrange towards the equilibrium excited state geometry where the rate of this rearrangement controlled by ion mobility. This creates peculiar PL color dependence for CuN4 in glass forming polymers that we visualize by plotting PL color as spectral intensity ratio (I(530)/I(610)) versus sample temperature (Figure 2C). Three distinct regions of the ratiometry29 curve describe the relation between temperature and ion pair motions in the polymer host. In a glassy environment the emission color varies monotonically until the polymer is sufficiently mobile to allow ion pairs to rearrange. This point is characterized by a distinct change in the PL spectrum showing a local maximum in the ratiometry curve that marks the onset of the mobility associated with glass transition, we will refer to this temperature as PL onset temperature Further increase in temperature accelerates the ion diffusion making it sufficiently fast to take place within the lifetime of the probe excited state. At this temperature the ratiometry curve recovers a positive slope which is marked by a local minimum that we previously referred to as the dynamic Tg as it occurred on characteristic timescales of microseconds.39

Our initial aim was to target CuN4 probes to the polymer end groups that can be done in a multi-step synthesis. We firstly prepared a series of chain end labelled poly(methyl acrylate) samples incorporating the N4 ligand at the chain end using RAFT polymerization technique (pMA-N4, Figure 1). The polymer samples of Mw, varying from 4 kDa to 53 kDa were further treated with Cu metal precursor to convert N4 ligand to luminescent copper complex (pMA-CuN4, Figure 1). NMR spectroscopy confirmed the identity of resulting species at every step of polymer synthesis indicating incorporation of macroyclic ligand at the terminal site of the pMA chain and its further conversion to the...
charged luminescent Cu complex (See Supporting Information). Post metalation, polymer samples were drop cast from solution, conditioned at T>Tg and the temperature dependence of their luminescence was analyzed.

We found the luminescence of all CuN4 labelled polymer samples was temperature dependent. We specifically noted the strong Mw dependence of probe luminescence in the glassy state. Comparing the PL spectra recorded at -90°C (Figure 2a), we observed significantly red shifted probe emission in low Mw polymers compared to that in high Mw samples. This color variation is somewhat unexpected as it occurs in a set of chemically identical polymers and emissive complexes of identical chemical structure.

Figure 2 (A) Molecular weight dependence of emission spectra of end-labelled pMA in the glassy state at -90°C; (B) Thermochromism of end labelled pMA with Mw=52.7 kDa at selected temperatures with wavelengths used for ratiometry analysis indicated λ=530 nm, 2P=610 nm; (C) Ratiometric data for pMA with Mw=52.7 kDa, duplicate measurements shown.

Rationalizing these PL differences we recall that PL color in CuN4 is controlled by the ion pair spacing,29-30 which suggests that pMA of different molecular weight confines the probe molecules differently. Specifically, the red shift of PL spectrum observed in low Mw pMA implies a more tight ion pairing compared to that in high Mw pMA. This indicates that the volume around the chain end available for confinement is lower in low Mw pMA and gradually increases with increase of Mw.

This directly links the observed probe confinement effects to the free volume characteristics of polymer glasses and implies that the free volume element (FVE) size in pMA is Mw dependent and decreases for higher Mw. While unusual, this idea finds support from literature suggesting that the FVE size does decrease with increasing molecular weight at least for polystyrene.31 In addition, the concept of packing density dependence on chain length is well documented on the macroscopic scale. For example, Zou et al. have drawn similarities between temperature dependence of Tg and chain packing density and using a macroscopic granular chain model demonstrated that higher density packings are indeed formed by shorter chains.32 Finally, the recent data from Fayer and co-workers suggests that CuN4 sensors might indeed occupy FVEs in the polymer. Authors found the sizes of FVE in PS and PMMA to span the range of 5-8 Å making them at least partially accessible for CuN4 probes sized in the same extent.33

Figure 3. Ratiometry data for end labelled pMA samples (A) and pMA blends with freely dispersed CuN4 probes (B); (C) Mw dependence of the probe mobilization onset temperature in these polymers; (D) DSC data for charged and neutral pMA samples and pMA/CuN4 blends indicating Tg perturbation; all lines to guide the eye.

Having observed that end group confinement in pMA is Mw dependent we expected similar differences in the probe mobilization dynamics. One would assume that reaching identical extent of probe mobility in a highly confined medium would require a higher temperature compared to the less confined packing. Indeed, analysis of the ratiometry data in Figure 3A points out that high Mw pMA permits chain end mobilization at significantly lower temperatures compared to low Mw pMA that has more confined chain end groups (Figure 3C). The onset of end-group mobilization in the pMA series varies from 28.0°C for the 3.9 kDa sample to 13.8°C for the 52.7 kDa sample with the latter value being similar to the bulk Tg measured using differential scanning calorimetry (DSC, Figure 3D). Notably the PL
onset temperatures, reflective of a local Tg in the chain end vicinity, scale monotonically with log(Mo) pointing to two separate features of the local chain end behavior. Firstly, to the apparent lack of correlation with entanglement Mn,34,35 and secondly, to a continuous nature of Mn dependence that contrasts the Tg saturation behavior implied by the Flory-Fox relations for the polymer bulk.

The differences we observed for local PL-based Tg also translate to the bulk of end-labelled pMA. The presence of a covalently linked large cationic Cu complex at the chain end perturbs the bulk Tg of these polymers (Figure 3D) that undergo glass transition at significantly higher temperature compared to their neutral counterparts (pMA-N4 vs pMA-CuN4, Figure 1 and 3D). At largest, the differences reach ca. 15 degrees as in the case of 3.9 kDa sample and in line with previous reports,20 they diminish upon increase of Mn when the chain end concentration decreases.

To check whether local and bulk Tg perturbations are correlated we prepared a sets of control pMA samples with probe molecules freely dispersed in the polymer. We expected that the free probe would be similarly capable of confining in pMA and demonstrate a local Tg trend similar to that of end-labelled samples. Indeed, the PL onset temperature for a free probe in pMA exhibits monotonic Mn dependence similar to that of the end labelled series (Figure 3B/C). The sole exception in this series is a low Mn sample where the FVE size might be too small to incorporate CuN4 probe. At the same time, addition of a freely dispersed probe did not perturb the bulk Tg of pMA. The data plotted in Figure 3D is similar to the reference pMA series with neutral end groups. This suggests that FVE size, its occupancy and probe confinement are likely to impact the bulk Tg only if a bulky end-group is covalently linked to the polymer chain.

Seeking to rationalize the importance of Mn dependent confinement for the bulk behavior we note the consistency of this idea with theories suggesting that the glassy polymers can experience caging effects where the onset of glass transition is marked by the ability of polymer fragment to leave the cage formed by its nearest neighbors.36 Similar analogies can be drawn with granular materials and macroscopic systems subject to jamming37-39 that might be behind the strong Tg perturbations observed for end labeled pMA samples with the highest degree of end group confinement. Finally, it is known that the presence of end groups can significantly alter the diffusion rates as shown by Matsushita and co-workers40 who analyzed diffusion rates in cyclic and linear polystyrenes. All the phenomena above can affect the polymer mobilization onset, thus affecting the bulk Tg in pMA series with covalently linked probe molecules.

Out data so far suggests that the ability of polymer of specific length to form voids and confine small molecules is a general behavior of a polymer governed by its Mn rather than being an artefact or consequence of probe incorporation. To verify this, we prepared a series of control samples by two- and tenfold dilution of the end-labelled pMA (8.2 kDa) with its neutral counterpart of similar Mn. We registered nearly identical ratiometric traces for these samples with PL onset temperatures for this dilution series similar within 1° despite probe concentrations varied tenfold (Figure S2.4). Additionally probe aggregation was ruled out using confocal lifetime imaging microscopy reporting no heterogeneities in pMA-CuN4 (Figure S2.7-2.8 in the Supporting Information). Taken together this data suggests that end group confinement and resulting Mn dependence of the probe mobilization dynamics might be a purely structural phenomenon.

If this suggestion is correct, then the structure and placement of the probe molecule should dramatically alter the local PL data registered in pMA, especially in the case of significant size mismatch or disruption of probe confinement. We tested this using two sets of controls with the first series featuring CuN4 probes attached randomly to the pMA chains. We observed no Mn dependence of the PL onset in this set of samples (Figure 4B and Figure S2.5 for ratiometry curves) confirming that the probe attached at random positions does not confine uniformly and remains insensitive to Mn variations. Similarly, such probe attachment does not increase the bulk Tg contrary to what was observed for the end-labelled pMA (Figure 4C).

**Figure 4.** (A) Solid state structures of small molecule probes with tetrafluoroborate and BARF counterions indicating their different sizes, structures adopted from Refs. 29-30; (B) Comparison of PL data for end- and side chain labelled pMA; (C) DCS data for these polymers compared to the neutral pMA-N4 reference.

Since packing voids in pMA have a finite size, the second set of controls was prepared to induce a size mismatch between the luminescent probe and FVE. We used a large CuN4-BARF probe (Figure 4A) that is ca 2nm in size – twice larger than CuN4-BF4 probe used throughout this work – a value exceeding pMA length of persistence.34-40 We found that the size mismatch induced by large probe renders
pMA/CuN₄-BARF blends entirely unresponsive - no ratiometric response to glass transition was found in samples where the large probe was freely dispersed (Figure S2.6). This suggests that confinements capable of incorporating the probe are generated by the polymer host rather than probe-induced.

Interestingly, the large BARF probe that was unresponsive in freely dispersed form, becomes sensitive to glass transition once linked to the polymer end group covalently (Figure 4B and S2.3). Likely due to its disturbed confinement, the PL onset for this sample series is largely M₆ independent. Due to its covalent attachment, the bulky BARF probe is capable of acting as diffusion constraint as it perturbs the bulk Tₘ by ca. 5 degrees similar to its smaller sized counterpart (Figure 4C).

Summarizing our observations we highlight two distinct phenomena revealed by the probe studies in pMA. Firstly, we find that pMA can apparently confine chain end groups and small emissive molecules dispersed in this polymer. The extent of confinement depends on molecular weight with low M₆ glasses providing more compact confinements that imply smaller FVE sizes in low M₆ polymers. We confirm that such confinement does not require covalent incorporation of the probe molecule but relies on the similarity between the probe size and that of FVE. Since the common end groups in synthetic polymers are smaller than CuN₄, we conclude that almost universally polymer end groups should experience these confinement effects.

We further show that end group size and structure are the likely causes of Tₘ perturbation observed in a number of previous reports. Based on our probe placement studies we link this perturbation to the chain ends acting as diffusion constraints that are affected by confinement effects expressed strongly in low M₆ glasses. This explains why low M₆ glasses are particularly susceptible to Tₘ perturbations due to end group structure variations. Ironically, this line of reasoning suggests that the largest Tₘ perturbation would result in the weakest log(M₆) dependence of the Tₘ making this effect easy to overlook unless it is intentionally investigated.

Finally, we highlight the capacity of environmentally sensitive emissive probes like CuN₄ to reflect the multitude of environments found in a simple linear homopolymer. We show how placement chemistry dramatically affects the probe behavior that in some cases renders the probe entirely unresponsive. We anticipate that with more advanced probe designs it should be possible to assess the structural aspects of probe behavior in a quantitative way.

In conclusion we note that placing emissive molecules in polymer glasses is arguably a common practice in a variety of fields. Numerous light generation applications involve using polymer glasses as dye hosts and characterizing emission of new luminescent compounds in PS or PMMA films is a regular practice in materials science. It is not uncommon for luminescence in glasses to differ from that in solution or pristine solid. Our work suggests that complex structural phenomena may be driving these differences. Namely, we show that a polymer glass is a highly irregular solvation medium offering a variety of voids and environments for luminophore incorporation that make the common view on luminescent compounds being simply dissolved in a polymer glass no longer valid. On the other hand, selective and structure-guided incorporation of luminophores opens up a new tool for designing emissive glassy materials where confinement effects and PL environmental sensitivity can tune the material performance via the productive interplay disclosed in this work.

ASSOCIATED CONTENT
Supporting Information contains synthesis details and full characterization data. It is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Linked probe: perturbs bulk Tg

Confined: Tg responsive

Mismatched: Tg silent

Polymer glass as a structurally diverse solvent
Supporting Information

Environmentally Sensitive Luminescence Reveals Spatial Confinement, Dynamics and Their Molecular Weight Dependence in a Polymer Glass

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S0. General considerations

All manipulations unless stated otherwise were performed using Schlenk or glovebox techniques under dry argon atmosphere. Anhydrous solvents were dispensed from an solvent purification system manufactured by INERT (USA) and degassed prior to use. Anhydrous deuterated solvents were purchased from Eurisotop, degassed and stored over 4Å molecular sieves. Methyl acrylate was passed through alumina plug, degassed and used immediately. AIBN initiator was recrystallized from warm diethyl ether before use. All other chemicals unless noted otherwise were purchased from major commercial suppliers (TCI Europe and Sigma-Aldrich) and used without purification.

Instrumentation and methods:

NMR spectra were measured on Agilent 400-MR DD2 spectrometer. LCMS measurements were performed using LTQ XL spectrometer equipped with Shimadzu HPLC setup operating at 0.2 mL/min flow rate with water/MeCN mobile phase containing 0.1% vol formic acid and Discovery C18 column. Gel permeation chromatography (GPC) measurements were performed using Shimadzu HPLC setup equipped with Agilent PLGel column operating at 40°C with THF as the mobile phase supplied at 1 mL/min flow rate. Quantification was performed using refractive index detector, the apparatus was calibrated using ReadyCal PMMA standards. Differential Scanning Calorimetry measurements were performed in crimped Al sample pans using a TA DSC250 and Perkin Elmer Pyris Diamond DSC apparatus operating at 20 °C/min ramp rate in dry nitrogen. Samples were conditioned at 75°C before the measurement for at least 10 minutes and subsequent 1st and 2nd heating curves were used to obtain average T_g value.

Photophysical characterization

The photoluminescence measurements were performed using Ocean Optics HDX spectrometer integrated in a free space optics assembly with excitation at 405 nm delivered by a ThorLabs laser module (CPS405).

IMPORTANT NOTE: The response of spectrometer was calibrated using reference light source (Ocean Optics, HL-3P-CAL) to deliver accurate absolute spectral intensity measurements. See the example of the influence on the processing routine below in S3.

Heating and cooling was performed in a modified Linkam THMS 600 stage flushed with nitrogen throughout the experiment to prevent icing.

Confocal microscopy measurements were performed using Leica SP8 DIVE apparatus using polymer samples drop cast on cover slips and treated as described below in S3.
S1. Synthesis and compound characterization

Macrocyclic ligand $N_4^{tBuBuOH}$:

Commercial pyridine dimethanol A (TCI) was converted to monoaldehyde B following the literature procedure\(^1\) that can be scaled up to 100 mmol. Oily B was found to solidify overtime without impairing its reactivity. All compounds described in this multistep synthesis were used without additional purification that was performed after the final cyclisation step.

Aminoalcohol C: 8.13 g of solidified aldehyde B (1eq., 59.3 mmol) were loaded in a round bottom flask containing 100 mL absolute methanol. No exclusion or air or moisture was necessary. The suspension was stirred vigorously and tert-butyl amine (2eq., 12.47 mL, 118.68 mmol) was added to the flask at room temperature in one portion. Within 20 minutes suspended aldehyde dissolved and IR indicated the consumption of the starting aldehyde. To the clear solution, solid NaBH$_4$ (3.6 g, ca. 1.6 eq.) was added in three portions over the period of 15 minutes and the bubbling solution was allowed to stir for additional 2 hours. Upon completion, reaction mixture was carefully (gas evolution!) quenched with saturated sodium bicarbonate solution (50 mL), diluted with water twofold and extracted with chloroform (5x50 mL). Combined organic phase was dried with potassium carbonate and concentrated to give 11.3 g of clear oil (>99%) that was used without additional purification.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.62 (t, $^3$$J_{HH} = 7.7$ Hz, 1H, py-p-CH), 7.24 (d, $^3$$J_{HH} = 7.8$ Hz, 1H, py-o-CH), 7.08 (d, $^3$$J_{HH} = 7.7$ Hz, 1H, py-o-CH), 7.08 (d, $^3$$J_{HH} = 7.7$ Hz, 1H, py-CH$_2$-OH), 4.71 (s, 2H, -CH$_2$-OH), 3.88 (s, 2H, -CH$_2$-NH$tBu$), 1.19 (s, 9H, $^1$Bu).
Figure S1.1. $^1$H NMR spectrum of aminoalcohol C in CDCl$_3$

Synthesis of aminoalcohol E:

Chloromethyl amine D: To 12 g (61.85 mmol) of amino alcohol C dissolved in anhydrous dichloromethane (60 mL), thionyl chloride (2 eq, 14.71 g, 8.97 mL, ca 123.7 mmol) were added dropwise using syringe over the period of three minutes under Ar flow. Reaction mixture was capped with oil bubbler and allowed to stir for 1.5 hours when NMR indicated the completion of reaction. Volatile compounds were removed by distillation under static vacuum into a liquid nitrogen cooled trap. Remainder of thionyl chloride was removed by two co-evaporations with 15 mL toluene done similarly, using distillation into the cold trap. This treatment yielded waxy solid that was further co-evaporated with acetonitrile to remove
trace amounts of water. Resulting product D was a hydrochloride salt that was used without isolation for the next step. NMR data below is presented for the hydrochloride salt in D$_2$O.

$^1$H NMR (400 MHz, D$_2$O): $\delta$ 7.97 (t, $^1$J$_{HH} = 7.8$ Hz, 1H, py-p-CH), 7.62 (d, $^1$J$_{HH} = 7.8$ Hz, 1H, py-o-CH), 7.51 ($^3$J$_{HH}$, J = 7.8 Hz, 1H, py-o-CH), 4.77 (s, 2H, -CH$_2$Cl), 4.40 (s, 2H, -CH$_2$-NH$_2$-tBu), 1.48 (s, 9H).

Figure S1.2. $^1$H NMR spectrum of hydrochloride salt D in D$_2$O

If necessary, the neutral D can be isolated in the following way: A portion of wax obtained as described above is dissolved in water, cooled down to 0°C and neutralized with saturated sodium bicarbonate solution. Aqueous phase is extracted three times with chloroform and organic phase is dried with solid K$_2$CO$_3$ and concentrated on the rotary evaporator while maintaining the bath temperature below 40°C to prevent alkylation side reactions. Neutralized compound D is obtained as clear oil that can be stored in the freezer (-20°C) for two days before notable degradation occurs. Due to the lack of long term stability, compound D was handled exclusively as HCl salt in all synthesis steps. NMR data for neutral D is given below:
\[1^1H \text{ NMR} \ (400 \text{ MHz, CDCl}_3): \ \delta \ 7.65 \ (t, \ J_{HH} = 7.7 \text{ Hz, } 1\text{H, py-p-CH}), \ 7.30 \ (m, \ 2\text{H, overlap of two doublets, py-o-CH}), \ 4.64 \ (s, \ 2\text{H, -CH}_2\text{-Cl}), \ 3.88 \ (s, \ 2\text{H, -CH}_2\text{-NH' Bu}), \ 1.18 \ (s, \ 9\text{H, } \text{tBu}). \]

\[1^3C \text{ NMR} \ (100 \text{ MHz, CDCl}_3, \ \text{all singlets}): \ \delta \ 160.46, \ 155.85, \ 137.38, \ 121.58, \ 120.72, \ 50.56, \ 48.31, \ 46.83, \ 29.09. \]

**Figure S1.3.** \[1^1H \text{ NMR spectrum of neutral D in CDCl}_3\]
Aminoalcohol $\text{E}$: To the waxy solid $\text{D}$ obtained as described above in hydrochloride form (ca. 61.85 mmol) was added 200 mL acetonitrile and a milky suspension was stirred for 5 minutes. A portion of solid finely ground $\text{K}_2\text{CO}_3$ (25.6 g, ca 3 eq.) was added to this suspension at 0°C and the reaction mixture was allowed to stir for 15 minutes to neutralize the HCl bound to compound $\text{D}$. Further, an aliquot of 2-amino-2-methyl-1-propanol (55 g, ca. 10 eq) was molten using heatgun (60°C) and slowly poured into the reaction mixture cooled to 0°C.

NOTE: Care should be taken to cool down reaction mixture as addition of amine to protonated compound $\text{D}$ was found to be highly exothermic and resulted in notable degradation.

After amine addition, reaction mixture was heated at 80°C for 8 hours and filtered to remove undissolved inorganic solids. Acetonitrile was removed using rotary evaporator and resulting thick oil was dissolved in water (200 mL) and extracted with chloroform (5x75 mL) leaving the majority of aminomethyl propanol in the aqueous phase. Organic phase was further washed with small (!) portions of water (3x5 mL) and brine (5 mL), dried over solid $\text{K}_2\text{CO}_3$ and concentrated to give thick oil weighing 17.68 g that was used for final synthetic step without additional purification.
NOTE: In case of notable degradation, target compound E can be distilled using short path distillation apparatus at 180°C (bath temperature) under vacuum (ca. 0.3 mbar). Distillation is efficient in removing oligomerized byproducts, however traces of unreacted aminomethyl propanol are more conveniently removed by extraction of chloroform solution of E with small portions of water.

1H NMR (400 MHz, CDCl₃): δ 7.57 (t, 3J_HH = 7.7 Hz, 1H, py-p-CH), 7.24 (d, 1H, overlap with chloroform, py-o-CH), 7.09 (d, 3J_HH = 7.7 Hz, 1H, py-o-CH), 3.87 and 3.84 (both s, both 2H, -CH₂-NHR), 3.34 (s, 2H, -C(CH₃)₂-C₂H₂-OH), 1.18 (s, 9H, tBu), 1.13 (s, 6H, -C(CH₃)₂-CH₂-OH).

Figure S1.5. 1H NMR spectrum of crude E in CDCl₃
17 g of aminoalcohol \( E \) (64.1 mmol) prepared as above was dissolved in 10 mL acetonitrile and set aside. Separately, solution of 2,6-bis(bromomethyl)pyridine (16.27 g, 61.4 mmol) was prepared in 65 mL warm acetonitrile. Solutions were quickly mixed and transferred to a dropping funnel fixed onto a round bottom flask containing suspension of 19.5 g \( \text{Na}_2\text{CO}_3 \) (183.9 mmol, ca. 2.85 eq) in 300 mL of acetonitrile preheated to 80°C. Solution of both compounds was added to the carbonate suspension dropwise over a period of 40 minutes and allowed to stir further at 80°C for three hours. During the addition, milky suspension forms and reaction mixture becomes notably turbid overtime.

Reaction mixture was further cooled to 0°C and worked up as follows:

Acetonitrile mother liquor, isolated by filtration, contained unreacted bromomethyl pyridine and trace amounts of target compound. Evaporation of acetonitrile yields thick oily residue that was set aside.

Filter cake residue was suspended in chloroform and shaken with water to remove inorganic salts. Chloroform fractions were concentrated to yield thick wax that was treated with 150 mL water and concentrated HCl (36%) until nearly complete dissolution occurred. This typically requires 65 mmol of HCl with final solution pH=3. Solution was further passed through paper filter, diluted to ca 250 mL and treated with solid potassium carbonate upon vigorous stirring until pH=8-9. This results in the formation of stable milky emulsion and deposition of heavy wax on the vessel walls. The wax was analysed by NMR spectroscopy and contained no target macrocycle. Contents of the vessel were carefully transferred to the separatory funnel making sure to discard waxy residues and transfer the emulsion phase exclusively. Emulsion was further extracted with chloroform (4x100 mL) and the organic phases were combined, dried over \( \text{K}_2\text{CO}_3 \) and concentrated on the rotary evaporator. The resulting paste was triturated with diethyl ether (2x15mL) to remove coloured impurities, rinsed with pentane and dried under vacuum to yield very fine white powder of target compound (4.78 g). Additional portion of the product can be recovered by repeated extraction.
(CHCl₃, 4x50 mL) of the remaining aqueous emulsion once after treatment of the latter with 2M NaOH till pH 12. This yields additional 1.4 g of target compound not requiring washing with ether or pentane.

Concentrated acetonitrile mother liquor and ether washings can be subjected to identical repeated workup to yield small portions of product.

Combined yield: 6.18 g (27.35 %)

**¹H NMR** (400 MHz, CDCl₃) δ 7.05 (t, ³JHH = 7.6 Hz, 2H, p-Py-CH), 6.72 (d, ³JHH = 7.7 Hz, 2H, m-Py-CH), 6.55 (d, ³JHH = 7.5 Hz, 2H, m-Py-CH), 3.98 (broad s, 8H Py-C₂H), 3.62 (d, ³JHH = 5.6 Hz, 2H, N-C((CH₃)₂(CH₂OH))), 1.97 (s, 1H, -OH), 1.32 (s, 9H, -tBu-CH₃), 1.30 (s, 6H, N-C((CH₃)₂(CH₂OH))).

**¹³C NMR** (100 MHz, CDCl₃) δ 160.39(s, Py-Cquart), 158.77(s, Py-Cquart), 135.39(s, Py-Cpara), 122.11(s, Py-Cmeta), 120.55(s, Py-Cmeta), 69.75(s, -CH₂-OH), 59.29(s, -C-(CH₃)₂(CH₂OH)), 58.54(s, Py-CH₂), 56.07(s, -C-(CH₃)₃), 55.94(s, Py-CH₂), 28.00(s, tBu-CH₃), 23.51(s, -C-(CH₃)₂(CH₂OH)).
Figure S1.6. $^1$H NMR spectrum of $\text{N}_4^{\text{tButBuOH}}$ in CDCl$_3$. 
Figure S1.7. $^{13}$C NMR spectrum of $\text{N}_4^{\text{Bu}1\text{Bu}OH}$ in CDCl$_3$. 
Figure S1.8. gHMOC spectrum of $N_d^{\text{BuOH}}$ in CDCl₃.
Figure S1.9. gCOSY spectrum of N₄[BusBuOH] in CDCl₃.
Synthesis of RAFT chain transfer agent (CTA-N₄): 

140 mg of macrocycle N₄ButBuOH (380 µmol) were combined with DDMAT² (152 mg, 1.1 eq., 417 µmol), DPTS³ catalyst (1 eq., 111 mg) in dry dichloromethane (5mL). The mixture was stirred until a homogeneous clear solution formed and solution of DCC (117 mg, 1.5 eq.) in 2 mL dichloromethane was added to the mixture in one portion at room temperature under argon. Within 30 minutes white precipitate forms and reaction mixture is allowed to stir overnight at room temperature. Upon completion, suspension was filtered and yellow organic fraction was shaken with 1N HCl followed by saturated sodium bicarbonate and brine. This treatment produces more white solid suspended in the organic phase that was treated with sodium sulfate, filtered and concentrated to dryness on the rotary evaporator to produce thick waxy solid. The solid was further purified by column chromatography on silica eluting with dichloromethane to remove neutral contaminations and DDMAT decomposition products followed by DCM/NEt₃ (100/1) to elute a yellow band containing the target compound. Combined fractions were concentrated in vacuo and recrystallized from pentane at -20°C to produce pale yellow microcrystalline powder of target compound. Yield: 120 mg (44%).

¹H NMR (400 MHz, C₆D₆) δ 6.91 (t, 3JHH = 7.6 Hz, 2H, p-Py-CH), 6.70 (m, overlap of two doublets, 4H, both m-Py-CH), 4.19 (s, 2H, N-C(CH₃)₂(CH₂ODDMAT)), 4.11 (apparent d, 8H, Py-CH₂-), 3.15 (t, J = 7.5 Hz, 2H, -S-CH₂-nC₁₁H₂₄), 1.66 (s, 6H, -O-C(O)-C(CH₃)₂-S-), 1.46 (q, 2H, -S-CH₂-CH₂-nC₁₀H₂₂), 1.40 – 1.03 (m, overlap of 'Bu-CH₃, N-C(CH₃)₂(CH₂ODDMAT)) and 9 counts of -CH₂- groups of C12 tail, 6H+ 9H + 18H), 0.92 (t, J = 6.7 Hz, 3H, C12 tail, terminal -CH₃).
$^{13}$C NMR (101 MHz, C$_6$D$_6$) $\delta$ 221.89 (thiocarbonate $C_9$), 172.07 (carbonyl $R_2C=O$), 159.64 and 159.40 (py-C$_{2,6}$), 134.70 (py-C$_4$), 121.46 and 121.32 (py-C$_{3,5}$), 71.29 (N$_4$ N-C((CH$_3$)$_2$(CH$_2$ODDMAT), 57.87 and 57.62 (py-CH$_2$), 57.34, 55.96 and 55.21 ($C_q$ of DDMAT and 'Bu of N4 macrocycle), 36.66 (-S-CH$_2$-nC$_{11}$H$_{24}$), 31.95 (*), 29.70 (*), 29.60 (*), 29.45(*), 29.42(*), 29.07(*), 28.80 (-S-CH$_2$-CH$_2$-nC$_{10}$H$_{22}$), 27.26(*), 25.12 (DDMAT – C(C$_{10}$H$_{22}$)), 23.93(*), 22.73(*), 13.98 (DDMAT terminal CH$_3$).

(*) remaining resonances of 'Bu fragment CH$_3$ groups and C$_{12}$ chain of DDMAT
Figure S1.10. LC-MS data for RAFT CTA-N₄.
Figure S1.11. $^1$H NMR spectrum of RAFT CTA-N$_4$ in C$_6$D$_6$.
Figure S1.12. $^{13}$C NMR spectrum of RAFT CTA-N$_4$ in C$_6$D$_6$. 
Figure S1.13. gHSQC NMR spectrum of RAFT CTA-N4 in C6D6.
Polymer synthesis:

NMR tube scale polymerization and metallaion procedure:

The following procedure describes the NMR follow up of polymerization and subsequent metallation of 3.9 kDa sample with the synthesis conditions for remaining polymers given below in Table S1.

10 mg of RAFT CTA-N₄ (13.98 µmol) were combined with AIBN (0.2 eq., 0.4 mg) and methyl acrylate (63.37 µL, RAFT/M=1/50). An aliquot of THF-d₈ (250 µL) was added and NMR spectrum was recorded (A, Figure S1.14 below). The tube was heated at 65 °C for 6 hours and polymerization took place as indicated by the consumption of starting material (86% conversion) evident from the NMR spectrum (B, Figure S1.14). At this point, a sample for GPC analysis and calorimetry was withdrawn from the tube and metallaion of the material was performed.

To this polymer solution, 1 eq. of [Cu(MeCN)₄]BF₄ was added as solution in deuterated acetonitrile (14 µmol in 100 µL) and the tube was shaken. Colour changed from pale yellow to orange and equivalent amount of 1,3-di-isopropylimidazolium-2-carboxylate (14 µmol in 100 µL MeCN) was added, reaction mixture changed colour to yellow and NMR spectrum was recorded (C, Figure S1.14 below) to confirm the formation of Cu complex.

Analysis of 2D data (Figure S1.15) was consistent with complexation and in line with previous studies on similar small molecule complexes with BF₄ and BARF counter ions⁴⁻⁵. Formation of copper complexes with BARF counterion was performed similarly using [Cu(MeCN)₄]BARF metal precursor instead.⁴
Figure S1.14. $^1$H NMR follow up of polymerization and metalation of 3.9 kDa sample in THF-d8. Triangles indicate N₄ macrocycle resonances.
Figure S1.15. gHMQC spectrum of metallated 3.9 kDa sample in THF-d8. Resonances of Cu complex labelled.
General procedure for large scale polymerization:
Having confirmed the adequacy of the synthesis strategy we performed the remaining polymerization reactions separately using conditions indicated in Table S1. Typical procedure:
A sample of RAFT agent and AIBN combined as stock solutions in DMF at the ratio of RAFT/AIBN=1/0.2 were added to and methyl acrylate monomer in a glass vial in the glovebox. Additional DMF was added to the mixture and the vial was capped with air tight PTFE lined cap and warmed to 65 °C overnight. Upon completion of polymerizations all samples appeared as soft non flowing pale yellow lumps. Dichloromethane was added to polymer samples to partially dissolve them and the volatile organic compounds including unreacted monomer and DMF were removed in vacuo using rotary evaporator. This treatment was followed by an overnight drying in the vacuum oven (10-15 mbar) at 65°C. Resulting polymers were stored in the glovebox under Ar and metallated using the procedure described above.

NOTE: NMR spectroscopy was used to confirm ligand incorporation as in the case of the tube-scale synthesis (See Figures S1.17-1.20 for related spectra). NMR was found unreliable for analysing ligand content via comparing integration of end group resonances to those of the main chain functionalities due to limited dynamic range of the instrument incapable of resolving end group species present is low concentrations. A more reliable value can be obtained using Mₙ data from GPC or from NMR spectroscopy data collected with internal standard, e.g. benzene, present in amounts similar to those of the end groups. Metal incorporation was performed in a procedure identical to described above using protic THF as solvent. Outcome of metatlation was verified using NMR spectroscopy.

Blank pMA samples: were prepared using the procedure described above using DDMAT methyl ester (methyl 2-(dodecylthiocarbonothioylthio)2-methylpropionate)⁶ as a chain transfer agent to exclude the presence of carboxylic acid groups that can affect probe molecule in blended materials.
Blends of blank pMA with CuN₄ probes with BF₄ and BARF counterions were prepared using 100 mg of the polymer dissolved in DCM containing 0.5 and 1 mg of the Cu probe for BF₄ and BARF correspondingly. Solutions were mixed thoroughly, drop cast and vacuum dried before tested as outlined above. GPC data for the blank pMA samples is given in Figure S1.16B below
### Table S1. Synthesis conditions and properties of pMA samples

| No. | Mn, kDa | PDI | Monomer: RAFT:AIBN | T, °C | MA, µL | Solvent, µL |
|-----|---------|-----|--------------------|------|--------|-------------|
| 1   | 3.9     | 1.2 | 50/1/0.2           | 65   | 63.37  | THF-d8, 400[a] |
| 2   | 8.2     | 1.37| 100/1/0.2          | 65   | 300.56 | DMF, 100    |
| 3   | 13      | 1.45| 150/1/0.2          | 65   | 253    | THF-d8, 400[a] |
| 4   | 17.5    | 1.60| 200/1/0.2          | 65   | 1065   | DMF, 650    |
| 5   | 26.9    | 1.59| 400/1/0.2          | 65   | 1065   | DMF, 650    |
| 6   | 52.7    | 1.64| 600/1/0.2          | 65   | 799    | DMF, 650    |

[a] NMR tube scale reaction

**Figure S1.16 A.** GPC traces of end-labelled polymers. Dashed line is for the blank pMA sample used in dilution experiments.
Figure S1.16 B. GPC traces of blank pMA sample used in CuN₄ blending experiments.

Figure S1.17. ¹H NMR spectrum of 8.2 kDa pMA sample before metalation in CDCl₃. Insert shows the resonances of N₄ macrocycle.
**Figure S1.18.** $^1$H NMR spectrum of 17.5 kDa pMA sample before metalation in CDCl$_3$. Insert shows the resonances of N$_4$ macrocycle.

**Figure S1.19.** $^1$H NMR spectrum of 26.9 kDa pMA sample before metalation in CDCl$_3$. Insert shows the resonances of N$_4$ macrocycle.
Figure S1.20. $^1$H NMR spectrum of 52.7 kDa pMA sample before metalation in CDCl$_3$. Insert shows the resonances of N$_4$ macrocycle.
**Figure S1.21.** Section of $^1$H NMR spectra of metallated polymers prepared using general procedure in DMF. Counterion - BF$_4$. Measurements performed in protic THF with THF-d$_8$ reference capillary.
**Figure S1.22.** Section of $^1$H NMR spectra of metallated polymers prepared using general procedure in DMF. Counterion – BArF. Measurements performed in protic THF with THF-d8 reference capillary.
Preparation of the randomly labelled pMA samples.

Monomer synthesis:

\[ \text{NEt}_3 \quad \text{DCM} \quad \text{OH} \quad \begin{array}{c} \text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\end{array} \quad \begin{array}{c} \text{O} \\
\text{Cl} \\
\end{array} \quad \text{N}_4 \text{acrylate} \]

was prepared in the following way: 480 mg of macrocycle \( \text{N}_4^{\text{tButBuOH}} \) (1.3 mmol, preparation above) were dissolved in dry dichloromethane (5mL) containing ca 363 \( \mu \text{L} \) trimethylamine (2 eq., 2.61 mmol). Solution was cooled to 0°C and 115.5 \( \mu \text{L} \) of distilled acryloyl chloride (1.43 mmol, 1.15 eq.) were added in one portion. Solution turned pale yellow, was allowed to warm to room temperature and stirred for 1 hour to complete the reaction.

Upon completion, 5 mL of water was added in air, followed by saturated sodium bicarbonate solution and reaction mixture was extracted with DCM (4x25 mL) and combined organic extract was dried over sodium sulphate containing 100 mg Norit carbon to remove coloured impurities. Evaporation of DCM and trituration of resulting oil with cold pentane yields 410 mg of \( \text{N}_4 \) acrylate as tan solid (74.7%).

\(^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.06 (t, \(^3\)J\(_{HH} \) = 7.7 Hz, 2H, \( p-\text{Py-CH} \)), 6.71 (m, overlap of two doublets, 4H, both \( m-\text{Py-CH} \)), 6.47 (d, \(^3\)J\(_{HH} \) = 17.3 Hz, 1H, \(-\text{CH}=\text{CH}_2 \)), 6.31 – 6.10 (m, 1H, \(-\text{CH} = \text{CH}_2 \)), 5.88 (d, \(^3\)J\(_{HH} \) = 10.4 Hz, 1H, \(-\text{CH}=\text{CH}_2 \)), 4.30 (s, 2H, \(-\text{CH} = \text{CH}_2 \)), 4.02 (br apparent d, 8H, \( \text{Py-CH}_2 \)), 1.39 (s, 6H, \(-\text{C}((\text{CH}_3)_2) \)), 1.31 (s, 9H, \( 1\text{Bu-CH}_3 \)).

\(^{13}\text{C} \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 166.18 (carbonyl \( \text{R}_2\text{C}=\text{O} \)), 159.45 and 158.86 (py-\( \text{C}_{2,6} \)), 135.27 (py-\( \text{C}_4 \)), 130.95 (acrylate \(-\text{CH} = \text{CH}_2 \), 128.50 (acrylate \(-\text{CH} = \text{CH}_2 \), 122.04 and 121.79 (py-\( \text{C}_{3,5} \)), 69.63 \( -\text{CH} = \text{CH}_2 \)), 57.95 and 55.84 \( (1\text{Bu quaternary C}) \), 57.84 and 57.72 (py-\( \text{CH}_2 \)), 27.70 \( (1\text{Bu-CH}_3 \), 24.23 \( -\text{N-C}((\text{CH}_3)_2)\text{CH}_2\text{O} \)).
Figure S1.23. LC-MS data for N₄ acrylate
Figure S1.24. $^1$H NMR spectrum of N$_4$ acrylate in CDCl$_3$
Figure S1.25. $^{13}$C NMR spectrum of N$_4$ acrylate in CDCl$_3$
Figure S1.26. HMQC spectrum of N₄ acrylate in CDCl₃
**Polymer synthesis and metalation:**

All polymers were prepared with N4 ligand loaded at 20 µmol/g pMA. Mn variation was set by the amount of CTA used in co-polymerization. The stock of N4 acrylate monomer in methyl acrylate (20 µmol/g MA: 36.2 g N4 acrylate in 4.5 mL MA) and cyanomethyl dodecyl trithiocarbonate (stock in THF-d8, 122.62 mg in 700 µL) as a RAFT CTA. Ratios and loadings are indicated in the table below. Small amount of THF-d8 was added and reaction mixture was sealed in a J. Young tube and placed under blue LED light (455 nm) overnight. NMR reported >95% monomer conversion in all cases and the resulting polymer was recovered from the tubes by dissolving in chloroform and evaporating all volatiles. See representative 1H NMR spectrum below.

**Table S2.** Synthesis conditions and properties of pMA samples copolymerized with N4 acrylate

| No. | Mn, kDa | PDI | MA:CTA molar ratio | CTA, mg | MA, mL | Solvent, µL |
|-----|---------|-----|--------------------|---------|--------|-------------|
| 1   | 8.57    | 1.10| 75/1               | 70.07   | 1.5    | THF-d8, 500 |
| 2   | 17.19   | 1.15| 150/1              | 35.04   | 1.5    | THF-d8, 400 |
| 3   | 34.12   | 1.13| 300/1              | 17.52   | 1.5    | THF-d8, 500 |

Randomly labelled pMA was metallated is procedure identical to that used for end-labelled polymers. Identical NMR spectra were obtained (See data below).
Figure S1.27. $^1$H NMR spectrum of 8.57 kDa randomly labelled pMA sample before metalation in CDCl$_3$. Insert shows the resonances of N$_4$ macrocycle. Integration reports N$_4$:CTA ratio of 7.79 vs loaded 7.74

Figure S1.28. $^1$H NMR spectrum of 17.19 kDa randomly labelled pMA sample before metalation in CDCl$_3$. Insert shows the resonances of N$_4$ macrocycle. Integration reports N$_4$:CTA ratio of 3.55 vs loaded 3.87
Figure S1.29. $^1$H NMR spectrum of 34.12 kDa randomly labelled pMA sample before metalation in CDCl₃. Insert shows the resonances of N₄ macrocycle. Integration reports N₄:CTA ratio of 1.64 vs loaded 1.93
Figure S1.30. Section of $^1$H NMR spectra of metallated randomly labelled polymers. Counterion – BF$_4$. Measurements performed in protic THF with THF-d$_8$ reference capillary.
Figure S1.31. GPC traces for N-pMA copolymer
S2. Photoluminescence, structural and thermal data

All polymer samples were vacuum dried for at least 12 hours before characterization and further annealed at 75°C to erase thermal history before PL measurements and calorimetry experiments.

Temperature dependent photoluminescence spectra were recorded with an interval of 15° upwards of -90°C.

IMPORTANT NOTE: Raw spectrometer output was used to analyse spectral intensity ratio defined as count ratio at 530 vs 610 nm and used in all ratiometry plots. The obtained value was later corrected for instrument sensitivity using absolute irradiance calibration. An example of the processing routine is given below in Figure S2.1. Representative temperature dependence of the whole spectrum is shown in Figure 2C of the manuscript.

![Figure S2.1. Comparison between PL spectra before and after absolute irradiance calibration and impact on ratiometry data.](image-url)
Transition temperature analysis:

Figure S2.2. Example of processing of ratiometry data shown in Figure 3A of the manuscript and 1st derivative plot used to determine the curve maxima.

T_g(PL) values were estimated from ratiometry data as a zero of the 1st derivative of the ratiometry curve. See Figure S2.2 for data given in Figure 2 of the manuscript.
Figure S2.3. Ratiometry data for end-labelled pMA samples containing 2nm BArF probe. Transition temperature data shown in Figure 3 of the manuscript.
Figure S2.4. Ratiometry data for end-labelled pMA samples containing BF₄ probe at multiple dilution levels. Parent 8.2 kDa end labelled sample was diluted with blank polymer of Mn=9.46 kDa prepared as described above.
DCS data for neutral and charged pMA samples.

| Sample                        | Tg onset 1, °C | Tg onset 2, °C |
|-------------------------------|----------------|----------------|
| **Neutral series pMA-N4**     |                |                |
| 3.9 kDa                       | -4.74          | -4.15          |
| 8.2 kDa                       | 6.42           | 6.57           |
| 13 kDa                        | 9.39           | 9.40           |
| 17.5 kDa                      | 9.77           | 9.79           |
| 26.9 kDa                      | 14.57          | 14.37          |
| 52.7 kDa                      | 16.37          | 16.79          |
| **BF₄ counterion series, pMA-CuN₄** |    |                |
| 3.9 kDa                       | 10.12          | 10.74          |
| 8.2 kDa                       | 12.61          | 12.68          |
| 13 kDa                        | 10.75          | 10.80          |
| 17.5 kDa                      | 11.83          | 11.66          |
| 26.9 kDa                      | 12.24          | 13.19          |
| 52.7 kDa                      | 16.08          | 16.35          |
| **BArF counterion series, pMA-CuN₄-BArF** | | |
| 8.2 kDa                       | 11.37          | 11.83          |
| 17.5 kDa                      | 15.25          | 15.37          |
| 26.9 kDa                      | 15.52          | 15.47          |
| 52.7 kDa                      | 15.52          | 15.18          |
| **CuN₄/pMA blends, BF₄ counterion** | | |
| 5.49 kDa                      | 1.81           | 1.90           |
| 11.40 kDa                     | 8.56           | 8.57           |
| 17.55 kDa                     | 10.49          | 10.55          |
| 32.75 kDa                     | 14.23          | 14.34          |
| 43.31 kDa                     | 12.78          | 12.85          |
| **CuN₄ randomly labelled pMA, BF₄ counterion** | | |
| 8.57 kDa                      | -3.50          | -3.47          |
| 17.19 kDa                     | 2.03           | 1.99           |
| 34.12 kDa                     | 8.68           | 8.54           |

**Table S3.** Tg data for duplicate measurements of neutral pMA samples and those metallated with Cu complex with different counterions.
Figure S2.5. Ratiometry data for randomly labelled pMA samples (pMA-N₄ copolymer) containing BF₄ probe.

Figure S2.6. Ratiometry data for CuN₄-BARF probe freely dispersed in pMA.
Microscopy data.

**Figure S2.7.** Laser scanning confocal microscopy image for end-labelled pMA sample of Mn=8.2 kDa. Excitation by multiphoton source at 800 nm, emission detection range 550-580 nm.
Figure S2.8. Laser scanning confocal microscopy image for end-labelled pMA sample of Mn=52.7 kDa. Excitation by multiphoton source at 800 nm, emission detection range 550-580 nm.
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