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Photoactivity and pH Sensitivity of Methyl Orange Functionalized Poly(Propyleneamine) Dendrimers

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ABSTRACT: For the first time a pH indicator that responds to two different external stimuli, i.e. pH and light, namely methyl orange, has been implemented in a dendrimer. Six generations (G0−G5) of methyl orange-functionalized poly(propyleneamine) dendrimers (“MO dendrimers”) have been synthesized and characterized using ^{1}H NMR, ^{13}C NMR, and MALDI−TOF mass spectrometry. Subsequently, the response of the MO dendrimers toward pH changes has been monitored using UV−vis spectroscopy and the photophysical properties have been investigated. Furthermore, the photoisomerization from *E* to *Z* and the thermal recovery from *Z* to *E*, have been studied using UV−vis and transient-absorption spectroscopy. Interestingly, the response of the MO units toward pH changes is found to be generation dependent. On the other hand, the photophysical properties are found to be similar for all generations, except for the ϵ value, which deviates significantly from the expected value in the case of G4 and G5. Also the isomerization processes show no generation dependence within the same solvent, but different rate constants for the *Z*/*E* isomerization have been observed for different solvents.

Introduction

The interest in dendrimers has grown enormously over the past 2 decades, since they present a new class of molecules with some unique properties, in particular those substituted with groups able to perform specific functions.[1] Of particular interest are dendrimers containing switchable units, where controlled interconversion between two stable states is possible using external stimuli such as light[2], protons,[3] or electrons.[4]

Less common are dendrimers containing functional groups at the periphery, which can respond to two different external stimuli, i.e., light and pH. This class of compounds not only can provide new information about the interactions within dendritic molecules, but also can produce materials with unique characteristics. Very suitable for this purpose is methyl orange, which is widely used as a pH indicator for titration in aqueous solutions, having a pH transition interval in water between pH 3.1 (red) and pH 4.4 (yellow) (pK_a = 3.46).[5] The clear color change observed at the transition point is the result of protonation at the azo moiety, leading to an azonium ion, which is stabilized by mesomery (Scheme 1).[6]

Methyl orange is not only a pH-sensitive but also a light-responsive molecule, since it contains a photoisomerizable azo moiety, which can be converted from the thermodynamically more stable *E* form into the *Z* form upon light excitation. Subsequently, the *Z* form will normally recover to the *E* form either thermally or photochemically (Scheme 1).[7]

Therefore, the double functionality with respect to light and pH of methyl orange, once attached at the periphery of a dendrimer, is an interesting tool to study the possible interactions within dendritic molecules.

Here we present the complete synthesis, including a full characterization with ^{1}H NMR, ^{13}C NMR, and MALDI−TOF mass spectrometry, and the photophysical properties of six generations (G0−G5) of methyl orange functionalized poly(propyleneamine)dendrimers (“MO dendrimers”). Furthermore, the solvent dependency of the photoisomerization and the thermal *Z* to *E* isomerization have been investigated, as well as the spectroscopic behavior as a result of the protonation at the azo moieties. This resulted in the case of the protonation in the finding of different properties for the higher generations (dendritic effects) as compared to methyl orange itself. The isomerization processes were found to be generation independent.

Six generations (G0−G5) of MO dendrimers have been synthesized through the reaction of the sulfonic acid chloride of methyl orange with amine-functionalized poly(propyleneamine) dendrimers.[8] Methyl orange itself could not be used as a model compound for this study because of its very different solubility properties as compared to the MO dendrimers. For this purpose, G0 has been synthesized, by reacting propylamine with the sulfonic acid of methyl orange, to create a good model compound containing the same sulfonamide group as the higher generations. The number of MO units increases from 1 in G0, 3 in G1, 8 in G2, 16 in G3, and 32 in G4 to 64 in G5 (Figure 1).

Photophysical Properties

The absorption spectra of G0−G5 show $\pi\pi^*$ bands at 305 nm and at 445 nm ($\epsilon \approx 25\,000$ M^{-1} cm^{-1}) characteristic of the *E*-MO units. The nπ^* band typical of azobenzene units[9] is not visible, because the more intense $\pi\pi^*$ band appears in the same spectral region

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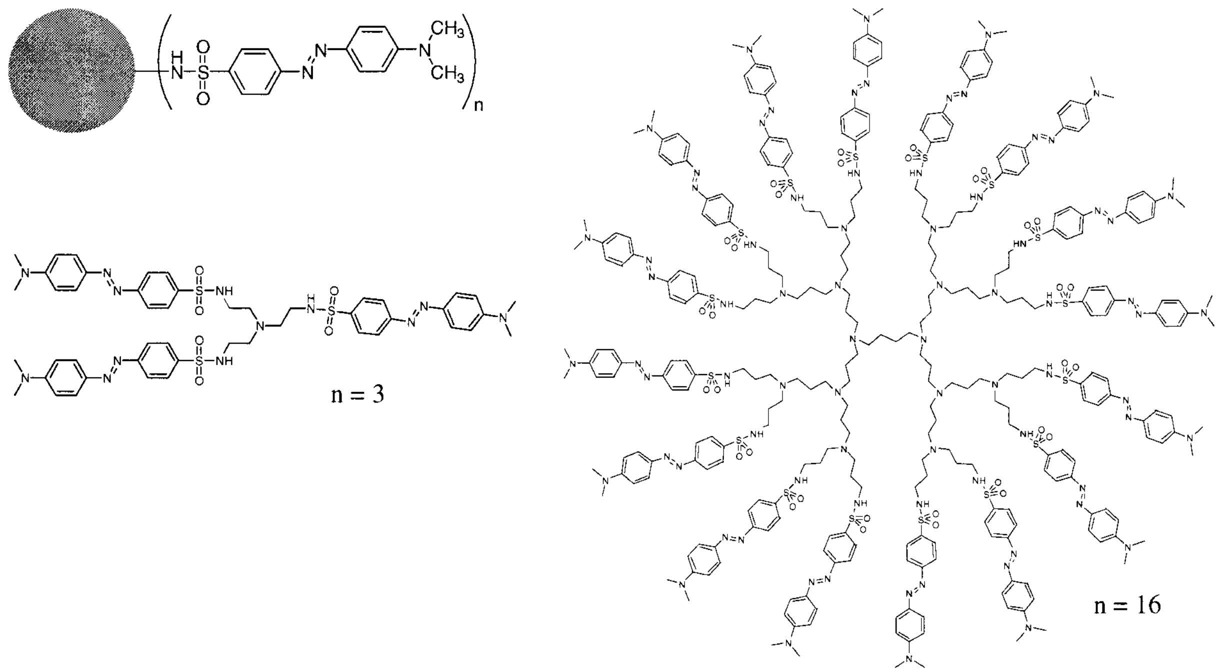
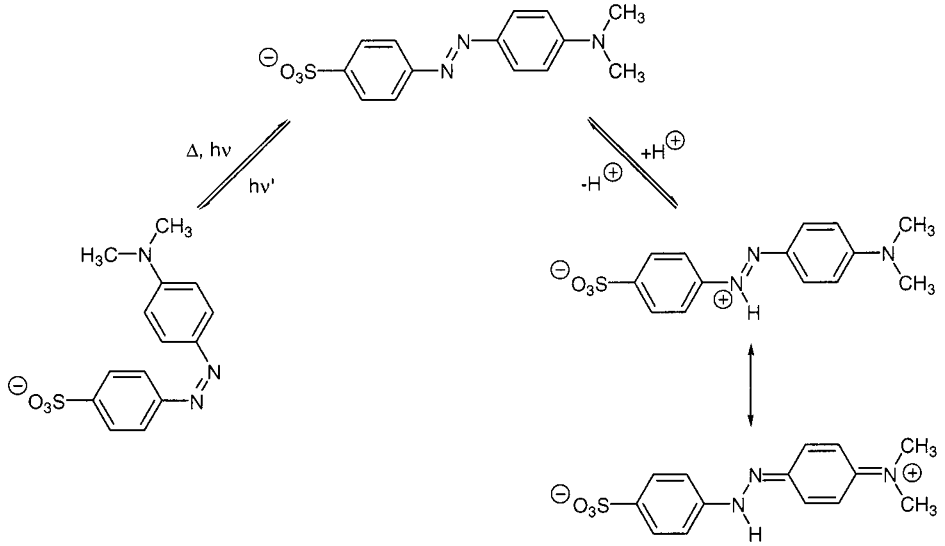


Figure 1. General depiction of the MO dendrimers bearing *n* MO units (*n* = 1, 3, 8, 16, 32, 64). Generations 1 (G1, *n* = 3) and 3 (G3, *n* = 16) are depicted in detail.

Scheme 1. Protonation to an Azonium Ion and the *E*/*Z*-Isomerization of Methyl Orange



(400−450 nm). It is interesting to notice that the ϵ values of the 445 nm band for G0−G3 are proportional to the number of MO units present in the dendrimer. However, for G4 and G5, the ϵ value shows a large deviation from the expected ϵ value, e.g., ϵ_{G5}(measured) = 1.09×10^6 M^{-1} cm^{-1} while ϵ_{G5}(expected) = 1.60×10^6 M^{-1} cm^{-1}. This rather large discrepancy could not be attributed to impurities or defects in the dendrimer[8] but is assigned to the locally high concentrations of MO units in the case of G4 and G5, which causes a deviation from the Lambert−Beer law, using identical MO unit concentrations for each generation.

Isomerization

Irradiation of a solution of a MO dendrimer in the spectral region between 440 and 480 nm results in the isomerization from the *E* to the *Z* form. The intensity of the $\pi\pi^*$ band at 445 nm decreases and a shoulder appears at 382 nm, corresponding to the $n\pi^*$ absorption band of the *Z* form (Figure 2). A photostationary state is reached for each generation after the flash, i.e., within a few nanoseconds, as proved by further irradiation, which does not result in a larger decrease of the $\pi\pi^*$ band or increase of the $n\pi^*$ band. An accurate evaluation of the percentage of photoisomerization was not possible, since the absorption spectrum of the *Z* form overlaps completely with the one of the *E* form. However, subtraction of the absorption spectrum of the photostationary state from the absorption spectrum of the *E* form gave a reasonable approximation for the absorption spectrum of the *Z* form (Figure 2). From the decrease in the $\pi\pi^*$ band at 445 nm the conversion of the *E* into the *Z* form is estimated to be higher than 35%.

To gain more insight in the isomerization of the MO units, both as a function of the solvent and as a function of the generation, the observed reaction rate (k_{obs} (s^{-1}))

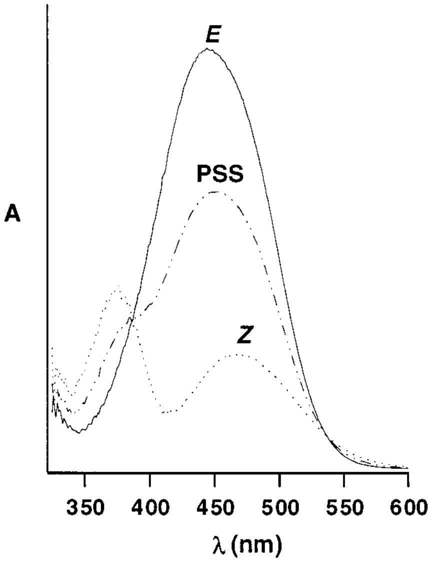


Figure 2. Absorption spectra of the *E* form, the photostationary state (PSS) and the predicted spectrum of the *Z* form.

Table 1. Observed Reaction Rates (k_{obs}) for the Thermal *Z*/*E* Isomerization in Various Solvents for G0−G5

	k_{obs} (10^{-3} s^{-1})			k_{obs} (s^{-1})
G	DCM/MeOH	DMF	DMSO	DMF/*N*MF[a]
0	46.94 ± 2.30	1.60 ± 0.10	4.71 ± 1.03	1.734 ± 0.025
1	68.17 ± 3.28	3.35 ± 0.49	7.23 ± 0.33	2.079 ± 0.102
2	66.59 ± 0.80	2.92 ± 0.22	9.14 ± 1.31	1.702 ± 0.107
3	50.17 ± 1.63	2.92 ± 0.16	6.47 ± 0.53	1.938 ± 0.144
4	63.39 ± 3.28	3.64 ± 0.22	6.15 ± 0.19	1.708 ± 0.026
5	45.66 ± 1.42	3.88 ± 0.22	7.13 ± 0.79	1.141 ± 0.122

[a] DCM = Dichloromethane; MeOH = methanol; DMF = *N,N'*-dimethylformamide; DMSO = dimethyl sulfoxide; *N*MF = *N*-methylformamide.

of the thermal recovery from the *Z* to the *E* form has been determined in various solvents for each generation (Table 1).

From this table can be seen that the *Z*/*E* isomerization in the dark is extremely fast as compared to azobenzene itself,[9] because the "push−pull" system formed by the NMe_2 group (electron donor) and the SO_2 group (electron acceptor) lowers the energy barrier for the isomerization process. The increase of k_{obs} with increasing polarity of the solvent is in agreement with the findings for the isomerization rates of azobenzenes with a "push−pull" system as previously described by Wildes et al.[10] Only the k_{obs} in 1/1 (v/v) DCM/MeOH is higher than expected. However, this may be attributed to the acidity of the solvent mixture, which makes the isomerization acid-catalyzed.

To gain more insight in the activation energy for the thermal *Z*/*E* isomerization, the temperature dependence of the observed rate constant has been measured for all generations in DMF. For each generation the rate of the *Z*/*E* isomerization is highly dependent on the temperature, but at a constant temperature, similar for G0−G5, which leads to an activation energy of ~ 64 kJ mol^{-1} for all generations. This value in fact is lower than the value of 94 kJ mol^{-1} found for the activation energy of the *Z*/*E* isomerization of azobenzene[10] itself, justifying the faster *Z*/*E* isomerization found for the MO dendrimers.

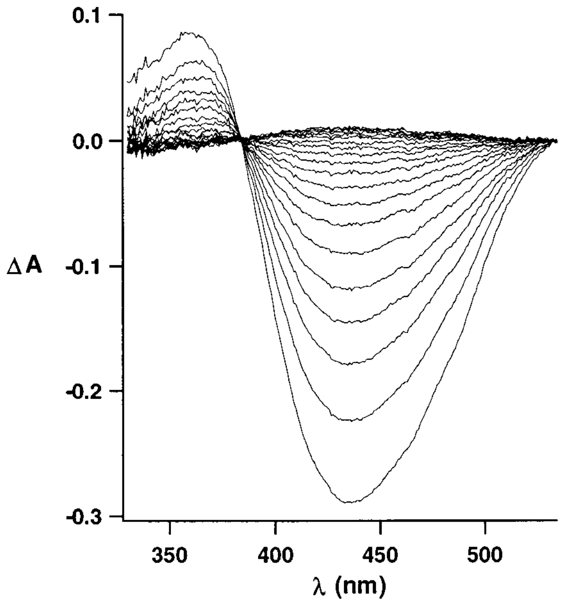


Figure 3. Transient-absorption spectrum of G1 in 1/1 v/v DMF/*N*MF. (λ_{exc} = 445 nm; inc. del. = 100 ms).

To follow the very fast *Z*/*E* isomerization in the 1/1 v/v *N*MF/DMF mixture transient absorption spectroscopy has been applied. The spectrum obtained just after the laser pulse clearly shows a bleaching in the 400−500 nm region due to the decrease of the $\pi\pi^*$ band at 445 nm of the *E* form as a result of the isomerization to the *Z* form. Furthermore, an increase in the absorption is observed at 380 nm, due to the stronger $n\pi^*$ absorption of the *Z* form (Figure 3).

For the other solvents a diode-array spectrophotometer was used to determine k_{obs}. All generations show a perfectly reversible photoisomerization and thermal back reaction during several cycles. The k_{obs} values measured for all generations are of the same order of magnitude within one solvent, so no strong dendritic effects are observed. This can only be the case when just a limited number of MO units isomerizes (only 35%) and when even in the higher generations a sufficient amount of free space is available for a MO unit to isomerize.

pH Sensitivity

Interestingly, protonation of the MO dendrimers at the azo moiety with trifluoroacetic acid (CF_3COOH) proceeds different for the lower generations (G0 and G1) as compared to the higher generations (G2−G5). Both G0 and G1 behave like the pH indicator, methyl orange itself, which means that the addition of acid causes a decrease in the $\pi\pi^*$ absorption band of the nonprotonated form at 445 nm and an increase in the $\pi\pi^*$ absorption band of the protonated form at 540 nm. The isosbestic point at 485 nm shows that this conversion from the nonprotonated to the protonated form is a clean reaction and that no degradation of the dendrimer takes place. However, in the case of the higher generations, the isosbestic point as present in G0 and G1 disappears and a new isosbestic point is found at shorter wavelength. Furthermore, the absorption band of the protonated form has become broader and less red shifted (see Figure 4).

The changes in the absorption spectra of G2−G5 upon protonation indicate that no longer all MO units can be protonated. So, the amount of charge that can be accumulated at the peripheral MO groups is less than expected due to the electrostatic repulsions between the positive charges already present in the dendrimer core. The broadening of the absorption spectrum of the

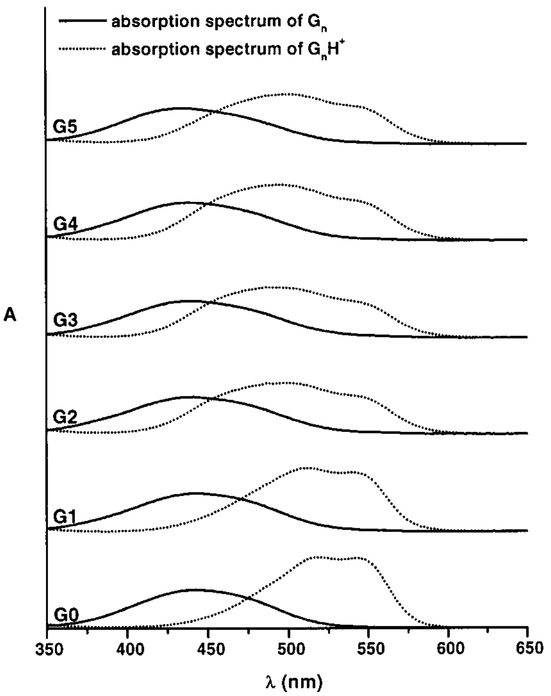


Figure 4. Absorption spectra of G*n* (straight line) and G*n*H$^+$ after addition of 100 μL of 0.5 M CF_3COOH (dotted line) in DCM ($n = 0, 1, 2, 3, 4, 5$).

protonated species may also be the result of sharing protons between two MO groups. In any case, after protonation of the tertiary amines in the interior of the dendrimer,[11] a large excess of acid is still necessary to induce the color change.

Furthermore, once the azo moiety of the MO groups is protonated to an azonium ion, emission is observed for all generations at 77 K with a maximum at 560 nm and a lifetime between 1.5 and 2 ns.

In summary, for the first time a photoresponsive pH indicator has been implemented in a dendrimer. All the described results show that the photophysical properties were found to be generation independent. Only the ϵ values of G4 and G5 show a significant deviation due to the locally high concentrations of MO units. Furthermore, both the *E*/*Z* and the *Z*/*E* isomerization rates are extremely high, though generation independent. The protonation behavior of the MO units indicates clearly that the higher generations of the dendrimer do not behave like methyl orange itself. In fact, the protonation is strongly influenced by the positive charges already present in the core and the color change is not so rapid and clear as indicated by the absorption spectra. Once the MO units are protonated, emission is observed at 77 K.

Experimental Section

Materials. Dichloromethane (DCM) (Uvasol, spectroscopic grade, Merck), methanol (MeOH) (Uvasol, spectroscopic grade, Merck), *N*,*N*′-dimethylformamide (DMF) (Uvasol, spectroscopic grade, Merck), dimethyl sulfoxide (DMSO) (Uvasol, spectroscopic grade, Merck), *N*-methylformamide (*N*MF) (99%, Aldrich), trifluoroacetic acid (99%, Acros Organics), phosphorus pentachloride (Merck), and methyl orange (Merck) were used as received. Amine-functionalized poly(propyleneamine)dendrimers, i.e., Astramol-$(NH_2)_n$ ($n = 3, 8, 16, 32, 64$), were obtained from Fa. BASF AG, Ludwigshafen, Germany.

Typical Synthesis Procedure for 16-Cascade:1,4-diaminobutane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidene)^3:*N*-[4-thiodioxo-4′-(dimethylamino)azobenzene] (MO Dendrimer G3). 16-cascade:1,2-diaminobutane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidene):(aminopropane) (101 mg, 0.06 mmol) and triethylamine (200 μL, 1.44 mmol) were dissolved in 50−100 mL of absolute chloroform. To this mixture was slowly added a solution of dabsyl chloride (332 mg, 1.03 mmol) in chloroform. The reaction mixture was refluxed for 5 days under argon. The solvent was removed in vacuo, and the residue collected in chloroform was washed with water, aqueous sodium carbonate, and again with water three times. After the organic phase was dried with sodium sulfate and evaporation of the solvent, the G3 was obtained as a red solid.

^{1}H NMR ($CDCl_3$): $\delta = 1.35-2.00$ (bm, 60H, $NCH_2CH_2CH_2N$), 2.10−2.75 (bm, 84H, NCH_2), 2.82 (b, 32H, CH_2NHSO_2), 2.94 (b, 96H, $N(CH_3)_2$), 6.56 (d, 32H, H3′ and H5′, $^3J_{HH} = 9.1$ Hz), 7.73 (d, 32H, H2′ and H6′, $^3J_{HH} = 9.1$ Hz), 7.76 (d, 32H, H2 and H6, $^3J_{HH} = 8.6$ Hz), 7.86 (bd, 32H, H3 and H5, $^3J_{HH} = 6.6$ Hz). ^{13}C NMR ($CDCl_3$): $\delta = 25.8$, 40.3, 51.6, 111.4, 122.6, 125.7, 128.1, 139.7, 143.6, 152.9, 155.3. MALDI−TOF MS *m*/*z* (%): 6284.3 (100, M + H$^+$), 3165.6 (62, M/2 + Na$^+$). Mp: 126−129 °C.

Characterization of *N*-Propyl[4′-(dimethylamino)azobenzene-4-sulfonic acid]amide (MO Dendrimer G0). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ [ppm] = 0.86 (t, $^3J_{HH} = 7.4$ Hz, 3 H, CH_3), 1.49 (sext, $^3J_{HH} = 7.4$ Hz, $^3J_{HH} = 7.2$ Hz, 2 H, $CH_2CH_2CH_3$), 2.94 (q, $^3J_{HH} = 6.8$ Hz, 2 H, $NHCH_2CH_2CH_3$), 3.05 (s, 6 H, NCH_3), 4.55 (t, $^3J_{HH} = 5.2$ Hz, CH_2NH), 6.75 (d, $^3J_{HH} = 9.1$ Hz, 2 H, ar. H), 7.92 (m, 6 H, ar. H). ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ [ppm] = 11.2 ($CH_2CH_2CH_3$), 23.1 ($CH_2CH_2CH_3$), 40.4 ($CH_2CH_2CH_3$), 45.1 ($N(CH_3)_2$), 111.6, 122.7, 125.8, 128.1 (CH, ar.), 139.6, 143.7, 153.2, 155.7 (C_q, ar.). EI−MS *m*/*z* (%): 346.2 (38, M $^+$), 148.1 (30, $Me_2NC_6H_4N_2{}^+$), 120.1 (100, $Me_2NC_6H_4{}^+$). Anal. Calcd for $C_{17}H_{22}N_4O_2S$ (MW 346.45). Mp: 182−184 °C.

Characterization of Tris[4′-(dimethylamino)azobenzene-4-sulfonic acid)-2-amidoethyl]amine (MO dendrimer G1). ^{1}H NMR (250 MHz, DMSO-d_6, 25 °C): δ [ppm] = 2.29 (bs, 6 H, $N(CH_2CH_2NHSO_2)_3$), 2.76 (bs, 6 H, $N(CH_2CH_2NHSO_2)_3$), 3.07 (s, 18 H, $(N(CH_3)_2)_3$), 6.81 (d, $^3J_{HH} = 9.2$ Hz, 6 H, ar. H), 7.58 (t, $^3J_{HH} = 5.3$ Hz, 3 H, 3 SO_2NH), 7.79−7.94 (m, 18 H, ar. H). ^{13}C NMR (62.9 MHz, DMSO-d_6, 25 °C): δ [ppm] = 52.0 $N(CH_2)$, 111.6, 122.3, 125.5, 127.7 (CH, ar.), 140.3, 142.6, 153.1, 154.5 (C_q, ar.). Positive FAB−MS, *m*-NBA, *m*/*z* (%): 1008.4 (59, M + H$^+$), 690.3 (40, M- $CH_2NHSO_2C_6H_4N{=}NC_6H_4\ N(CH_3)_2{}^+$), 224.1 (100, $C_6H_4N{=}NC_6H_4\ N(CH_3)_2{}^+$). Anal. Calcd for $C_{48}H_{57}N_{13}O_6S_3$ (MW 1008.24). Mp: 138−143 °C.

Characterization of 8-Cascade:1,2-diaminoethane-[4-*N*,*N*,*N*’,*N*’]:(1-azabutylidene)^2:*N*-[4-thiodioxo-4′-(dimethylamino)azobenzene] (MO dendrimer, G2). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ [ppm] = 1.11−1.48 (bm, 24 H, $NCH_2CH_2CH_2N$), 1.95−2.35 (bm, 36 H NCH_2), 2.65−2.85 (b, 16 H, CH_2NHSO_2), 3.10 (s, 48 H, $N(CH_3)_2$), 6.78 (d, 16 H, 8 H-3′ and 8 H-5′, $^3J_{HH} = 8.9$ Hz), 7.60−7.72 (b, 8 H, Amide-H), 7.80 (d, 16 H, $^3J_{HH} = 8.9$ Hz, H-3, H-5), 7.9 (s, 32 H, H-2, H-2′, H-6, H-6′). ^{13}C NMR (100.6 MHz, DMSO-d_6, 25 °C): δ [ppm] = 23.5, 26.4, 40.9, 50.5, 51.2, 111.3, 122.1, 125.3, 127.6, 140.1, 142.5, 152.8, 154.3. Positive FAB−MS, *m*-NBA, *m*/*z* (%): 1509 (7, M/2 − CH_2 + H$^+$). MALDI−TOF−MS, matrix HAB, *m*/*z* (%): 1509.8 (100, M/2 − CH_2 + H$^+$). Anal. Calcd for $C_{150}H_{196}N_{38}O_{16}S_8$ (MW 3043.92). Mp: 120−122 °C.

Characterization of 32-Cascade:1,4-diaminobutane-[4-*N*,*N*,*N*’,*N*’]:(1-azabutylidene)^4:*N*-[4-thiodioxo-4′-(dimethylamino)azobenzene] (MO dendrimer, G4). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ [ppm] = 0.70−1.10 (b, 124 H, $NCH_2CH_2CH_2N$), 1.30−1.95 (b, 180 H, NCH_2), 2.15−2.25 (b, 64 H, CH_2NHSO_2), 2.38−2.52 (b, 192 H, $N(CH_3)_2$), 6.10−6.30 (b, 64 H, 32 H-3′ and 32 H-5′), 7.05−7.25 (bm, 96 H, 32 Amide-H, 32 H-3 and 32 H-5), 7.26−7.45 (b, 124 H, je 32 H-2, H-2′, H-6, H-6′). ^{13}C NMR (100.6 MHz, DMSO-d_6, 25 °C): δ [ppm] = 26.0, 40.8, 50.3, 50.8, 111.3, 122.1, 125.3, 127.6, 140.0, 142.5, 152.8, 154.3. Anal. Calcd for $C_{632}H_{848}N_{158}O_{64}S_{32}$ (MW 12708.6). Mp: 129−132 °C.

Characterization of 64-Cascade:1,4-diaminobutane-[4-*N*,*N*,*N*’,*N*’]:(1-azabutylidene)^5:*N*-[4-thiodioxo-4′-(dimethylamino)azobenzene] (MO dendrimer, G5). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ [ppm] = 0.98−1.56 (b, 252 H,

$NCH_2CH_2CH_2N$), 1.63−2.34 (b, 372 H, NCH_2), 2.56−2.72 (b, 128 H, CH_2NHSO_2), 2.84−3.10 (b, 384 H, $N(CH_3)_2$), 6.39−6.71 (b, 128 H, 32 H-3′ and 32 H-5′), 7.40−7.87 (bm, 448 H, 64 Amide-H, 384 ar. H). ^{13}C NMR (100.6 MHz, DMSO-d_6, 25 °C): δ [ppm] = 26.4, 40.9, 50.6, 51.2, 111.5, 122.1, 125.3, 127.7, 140.0, 142.5, 152.7, 154.3. Anal. Calcd for $C_{1272}H_{1712}N_{318}O_{128}S_{64}$ (MW 25557.4). Mp: 155−158 °C.

Detailed information on the synthesis MO dendrimers can be obtained as Supporting Information.

NMR Spectroscopy. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer at 400 and 100.6 MHz, respectively.

FAB Mass Spectrometry. FAB mass spectra were recorded on a Concept 1H (Kratos Analytical Ltd., Manchester, England), using *m*-nitrobenzoicacid (*m*-NBA) as a solvent.

MALDI—TOF Mass Spectrometry. MALDI−TOF mass spectra were recorded on a TofSpec E (Micromass, Manchester, England). A 4-hydroxy azobenzene (HAB) matrix was used and the molecules were protonated with HCl.

UV—Vis Spectroscopy. Absorption spectra were recorded on a diode-array HP8453 spectrophotometer at 298 K.

pH Sensitivity. To a solution of a G*n* MO dendrimer (n = 0, 1, 2, 3, 4, 5) in DCM a 0.05 M solution of CF_3COOH in DCM was added in portions of 10 μL. After the addition of 70 μL, titration was continued with a 0.5 M solution of CF_3COOH in DCM to ensure full protonation. The concentration of methyl orange units was 1.20×10^{-5} M for all generations.

Fluorescence Measurements. Emission spectra were recorded on a SPEX fluorometer, irradiating the protonated MO dendrimers with 490 nm light in a 1/1 v/v DCM/MeOH glass at 77 K. The concentration of the methyl orange units was 2×10^{-6} M for all generations. The lifetime of the emission at 77 K was determined with single photon counting using a picosecond laser.

Kinetics of the *Z* to *E* Isomerization. Irradiation of the dendrimer solutions occurred in a closed spectrophotometric cell (volume 3 mL; optical path 1 cm) using a Yashica CS-201 auto flash from a camera. The concentration of methyl orange units was 1×10^{-5} M. Solutions were prepared in 1/1 v/v DCM/MeOH, DMF, DMSO, and 1/1 v/v DMF/*N*MF. The kinetics of the thermal *Z* to *E* isomerization were carried out on a HP8453 spectrophotometer. Spectra were recorded every second after irradiation, and from the recovery of the absorption at 445 nm, the rate of the thermal *Z*/*E* isomerization (k_{obs}) could be directly determined. Very fast isomerization processes were monitored via transient absorption using a ns YAG laser with an OMA detection system. In this case the sample was irradiated using 445 nm laser light.

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Supporting Information Available: Text giving the syntheses of the methyl orange-substituted dendrimers (G0−G5), a figure giving an Arrhenius plot, and a table showing the temperature dependence of the k_{obs} for G1−G5. This material is available free of charge via the Internet at http://pubs.acs.org.

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