J. Am. Chem. Soc. **1995,** *117,* 1754−1758

Aggregation in Fluid Solution of Dendritic Supermolecules made of Ruthenium(II)− and Osmium(II)−Polypyridine Building Blocks

Sebastiano Campagna,[*,1a] **Antonino Giannetto,**[1a] **Scolastica Serroni,**[1a]
Gianfranco Denti,[1b] **Sebastiano Trusso,**[1c] **Francesco Mallamace,**[1d] **and**
Norberto Micali[*,1c]

Contribution from the Dipartimento di Chimica Inorganica, Analitica e Struttura Molecolare dell'Università, via Sperone 31, I-98166 Vill. S. Agata, Messina, Italy, Laboratorio di Chimica Inorganica, Istituto di Chimica Agraria dell'Università, via S. Michele degli Scalzi 2, I-50124 Pisa, Italy, Dipartimento di Fisica dell'Università, via Sperone 31, I-98166 Vill. S. Agata, Messina, Italy, and Istituto di Tecniche Spettroscopiche del CNR, via Sperone 31, I-98166 Vill. S. Agata, Messina, Italy

Received June 14, 1994[®]

Abstract: Elastic and quasi-elastic light scattering and conductivity experiments have been performed on the supramolecular species $[Ru\{(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2\}_3](PF_6)_{20}$, **1**, and $[Os\{(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2\}_3](PF_6)_{20}$, **2**, in dilute fluid solution at room temperature (bpy = 2,2′-bipyridine; 2,3-dpp = 2,3-bis(2-pyridyl)pyrazine). Aggregation phenomena occur in fluid solution for **1** and **2** even at concentrations as low as 10^{-6} M. The dimension of the aggregates at 298 K in a 10^{-6} M acetonitrile solution is about 100 nm. The effects of ionic strength and solvent polarity on the aggregation are discussed. Intermolecular attractive interactions between the hydrophobic aromatic moieties of the supermolecules are likely at the basis of the aggregation process. The results obtained indicate that the nanometer-sized hyperbranched supermolecules investigated here can be considered as colloidal systems as far as the aggregation properties are concerned.

Introduction

Design and synthesis of ultralarge supramolecular species (nanostructures) capable of exhibiting specific functions is an important challenge now facing chemistry.[2] *Well-defined* nanometric species can be obtained by the "cascade approach"[3] (hyperbranched molecules, also called cascade molecules, dendrimers, or arborols) and can be considered as a bridge between molecular and material sciences.[4] Properties and new applications of these species are only beginning to be explored.[3c,e,4c,d]

On the other hand, it is known that various nanometer-sized species, such as microemulsion, micelles, silica particles, and biological macromolecules, can organize themselves in semimacroscopic edifices in solution.[5,6] For example, latex particles of 80 nm diameter at a volume fraction of 10^{-5} in water and a salt concentration of 10^{-2} M give rise to formation of clusters in which the internal structure is self-similar (fractal dimension, 2.1) and the dynamics are governed by reaction limit aggregation.[5,6] For ternary microemulsions (decane/water/dodecyl sulfoxysuccinate), the growth of percolation clusters with fractal dimension 2.5 is observed as a function of temperature. The size of the clusters can reach a fraction of a micrometer, while the dimensions of the droplets are on the order of 10 nm.[5,6] Biological macromolecules in water solution (e.g., lysozima, BSA, DNA) show aggregation phenomena, and the structure exhibits a diffusion-limited cluster−cluster aggregation (fractal dimension, 1.75).[5,6]

Some of us have recently prepared nanometer-sized hyperbranched supermolecules made of Ru(II) and Os(II) building blocks which exhibit quite interesting photophysical and electrochemical properties.[3d,7] Here, we report the aggregation properties in acetonitrile at very low concentrations of two representative species of this family of compounds, studied by laser light scattering and conductivity experiments. The reported investigation concerns the decanuclear species $[Ru\{(\mu\text{-}2,3\text{-dpp})\text{-}$

[®] Abstract published in *Advance ACS Abstracts,* January 1, 1995.

[1] (a) Dipartimento di Chimica Inorganica, Università di Messina. (b) Istituto di Chimica Agraria, Università di Pisa. (c) ITS-CNR, Messina. (d) Dipartimento di Fisica, Università di Messina.

[2] (a) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89. (b) *Molecular Electronic Devices*; Carter, F. L., Siatkowski, R. E., Woltjen, H., Eds.; North Holland: Amsterdam, 1988. (c) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304. (d) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312. (e) Ball, P.; Garwin, L. *Nature* **1992**, *355*, 761.

[3] (a) Buchlein, E.; Wehner, W.; Vögtle, F. *Synthesis* **1978**, 155. (b) Newkome, G. R.; Baker, G. R.; Saunders, M. J.; Russo, P. S.; Gupta, V. K.; Yao, Z.; Miller, J. E.; Bouillon, K. *J. Chem. Soc., Chem. Commun.* **1986**, 752. (c) Tomalia, D. A.; Naylor, A. M.; Goddard, W. G., III *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138. (d) Serroni, S.; Denti, G.; Campagna, S.; Juris, A.; Ciano, M.; Balzani, V. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1493. (e) Miller, T. M.; Neenan, T. X.; Zayas, R.; Blair, H. E. *J. Am. Chem. Soc.* **1993**, *115*, 356. (f) Mourey, T. H.; Turner, S. R.; Rubinstein, M.; Fréchet, J. M. J.; Hawker, C. J.; Wooley, K. L. *Macromolecules* **1992**, *25*, 2401.

[4] (a) Mekelburger, H.-B.; Jaworek, W.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1571. (b) Kim, Y. H. *Adv. Mater.* **1992**, *4*, 764. (c) Hodge, P. *Nature* **1993**, *362*, 18. (d) Dagani, R. *Chem. Eng. News* **1993**, *71* (4), 28. (e) Fréchet, J. M. J. *Science* **1994**, *263*, 1710.

[5] (a) Mallamace, F.; Micali, N. *Croat. Chem. Acta* **1992**, *65*, 379. (b) Magazù, S.; Maisano, G.; Mallamace, F.; Micali, N. *Phys. Rev. A* **1989**, *39*, 4195. (c) Mallamace, F.; Micali, N. *Long-Range Order in Disperse Systems*; La Rivista del Nuovo Cimento, Società Italiana di Fisica: Bologna, 1992.

[6] (a) Majolino, D.; Mallamace, F.; Migliardo, P.; Micali, N.; Vasi, C. *Phys. Rev. A* **1989**, *40*, 4665. (b) Bolle, G.; Cametti, C.; Codastefano, P.; Tartaglia, P. *Phys. Rev. A* **1987**, *35*, 837. (c) Cametti, C.; Codastefano, P.; Tartaglia, P. *Phys. Rev. A* **1987**, *36*, 4916.

[7] (a) Serroni, S.; Denti, G.; Campagna, S.; Ciano, M.; Balzani, V. *J. Chem. Soc., Chem. Commun.* **1991**, 944. (b) Denti, G.; Campagna, S.; Serroni, S.; Ciano, M.; Balzani, V. *J. Am. Chem. Soc.* **1992**, *114*, 2944, and references therein.

0002-7863/95/1517-1754$09.00/0

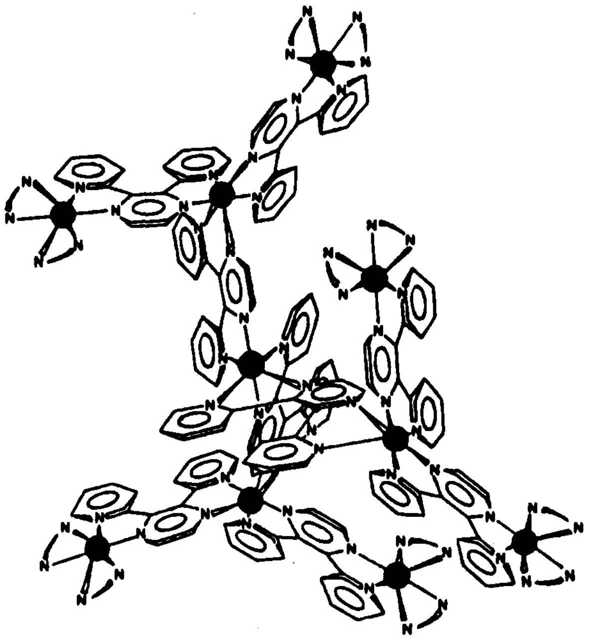

Figure 1. Schematic representation of the decanuclear species **1** (N⌒N stands for 2,2′-bipyridine; solid circles are Ru^{2+} metal ions). The hexafluorophosphate counterions are not represented.

$Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2\}_3](PF_6)_{20}$, **1**, and $[Os\{(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2\}_3](PF_6)_{20}$, **2** (Figure 1: bpy = 2,2′-bipyridine; μ-2,3-dpp = 2,3-bis(2-pyridyl)pyrazine).

The results show that supermolecules like those studied here can be considered as colloidal systems as far as their aggregation properties are concerned.

Experimental Section

$[Ru\{(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2\}_3](PF_6)_{20}$ (**1**), $[Os\{(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2\}_3](PF_6)_{20}$ (**2**), and $[Ru(bpy)_3](PF_6)_2$ were available from previous work.[7]

Conductivity experiments were performed in acetonitrile solution at 298 K on freshly prepared solutions (within one hour from the preparation of the solutions) and repeated on one-day aged solutions. The concentration range of the decametallic species was 2.5×10^{-7} to 4.0×10^{-4} M (5.0×10^{-6} to 8.0×10^{-3} N). Each set of experiments was repeated twice on different solutions, giving the same results.

The laser light-scattering measurements were made on at least one-day-aged solutions at 298 K in an optical thermostat (temperature stability, ±0.01 °C). The experiments were repeated after a few days, giving the same results. This ensured that thermodynamic equilibrium was achieved. The light source was a 10-mW He–Ne laser (wavelength 632.8 nm). A computerized goniometer was used to change the scattering angle. The light scattered by the systems was collected with appropriate optics and measured with a fiber-optic-coupled photomultiplier which gives a pulse rate proportional to the number of scattered photons. Malvern 4700 submicrometer particle analyzer correlator operating in parallel mode (8 parallel correlator at different sampling times) was used to obtain the correlation function $g_2(t)$ in the range between 10 μs and 0.6 s. All the samples (and pure solvents) were centrifuged prior to measurement. Due to the high molar extinction coefficients of **1** and **2** (e.g., $\epsilon = 125\,000\ M^{-1}\ cm^{-1}$ at 540 nm for **1**[7]), only dilute solutions (10^{-6} M) were studied by scattering techniques. Each set of experiments was repeated at least twice using ultrapure solvents of different grades (spectrophotometric or better) and origins, giving the same results within experimental error. This indicated that different water contamination in acetonitrile has no significant effect on light scattering results.

Results and Discussion

A. Laser Light Scattering. 1. Quasi-Elastic Light Scattering.

Quasi-elastic light scattering (QELS) experiments are used to determine the diameter of submicrometric dispersed particles by measurement of their diffusion coefficient.[8] The technique is based on the determination of the correlation function of the scattered light intensity, $g_2(t)$, by eq 1, where $\mathbf{q}$ is a function of the scattering angle θ, the refractive index n, and the wavelength of the incident light λ, and D is the diffusion coefficient of the particles.

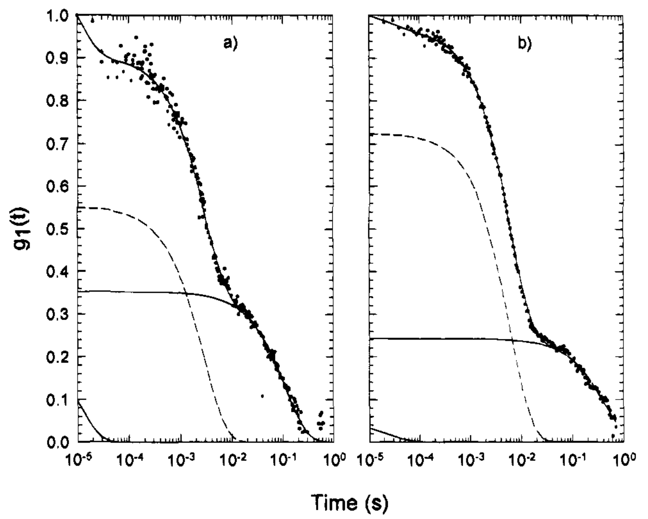

Figure 2. Field correlation functions $g_1(t)$ at finite ionic strengths at the scattering angle of 30° for **1** (a) and **2** (b). For details, see text.

$$g_2(t) \propto \exp(-2D\mathbf{q}^2 t) \tag{1}$$

$$\mathbf{q} = 4\pi n/\lambda \sin(\theta/2) \tag{1'}$$

The diameter of the particles (twice the hydrodynamic radius ϱ) can then be achieved by the use of the Einstein–Stokes relationship expressed by eq 2,

$$D = (k_B T)/(6\pi\eta\varrho) \tag{2}$$

where η is the viscosity of the solvent and k_B and T have the usual meanings. For polydispersed samples, $g_2(t)$ is a superposition of exponentials with different decay rates. Distribution of decay rates is then obtained by performing a Laplace inversion of the field correlation function $g_1(t) = [g_2(t)]^{1/2}$.

Here, we made use of the CONTIN program,[9] a non-negative least-squares algorithm, and a discrete multiexponential least-squares fit to invert the experimental data. All methods give a single peak for the size distribution function, with substantially good agreement. It was possible to observe a small contribution in the $g_2(t)$ function (at very short times and for solutions at low ionic strength) that can be related to isolated molecules, but this contribution was not analyzed because its amplitude was small compared to the principal relaxation time. The measurements were performed at scattering angles of 30, 40, and 70° (three different exchanged wave vectors $\mathbf{q}$) in order to test the $\mathbf{q}$ independence of the diffusion coefficient, D. When such a condition is proved, the measured relaxation time can be connected to the translational dynamics of the supramolecular aggregates, and eq 2 gives a corrected value for the size of the particle. At particular salt concentrations, the QELS measurements cannot be performed due to the low intensity of the signal.

Parts a and b of Figure 2 show field correlation functions $g_1(t)$ at finite ionic strengths at a scattering angle of 30° for **1**

---

(8) (a) Berne, B. J.; Pecora, R. *Dynamic Light Scattering*; Wiley: New York, 1976.

(9) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 213. We thank S. W. Provencher for provision of the Fortran program.

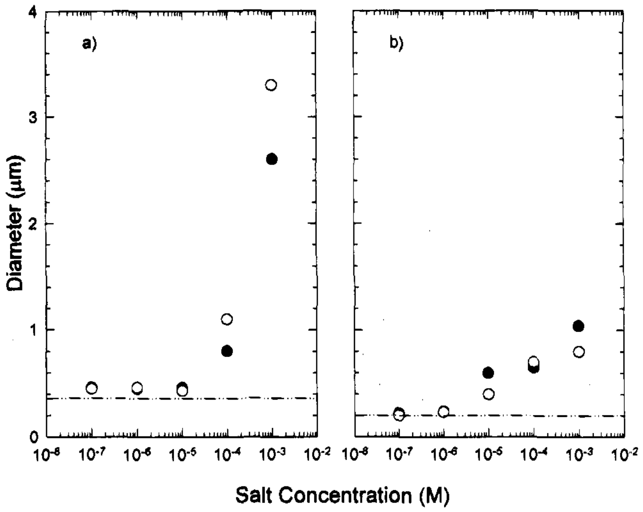

Figure 3. Mean diameters of **1** (a) and **2** (b) as a function of the molar concentration of added tetraethylammonium perchlorate (TEAP). Solid and open circles refer to different scattering angles (30 and 40°, respectively).

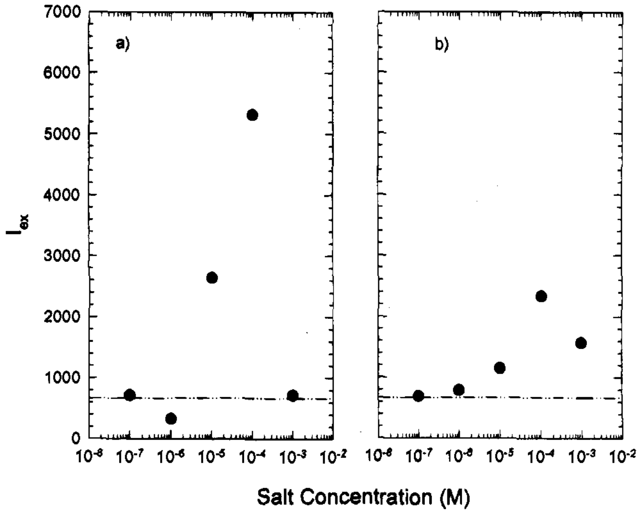

Figure 4. Excess light scattering intensity as a function of added TEAP for **1** (a) and **2** (b). The dashed horizontal line is the excess scattering intensity for samples without added salt.

and **2**, respectively. At very short times it is possible to observe the contribution from isolated molecules. The contribution at very long times (>0.1 s) is the same for all the samples and solvent and can, therefore, be assigned to impurities of the solvent and/or the stability of laser. The overall data are fitted by a three-exponential curve (solid line in Figure 2). Dashed lines in Figure 2 shows the contribution for intermediate times, giving the translational motion of the aggregates.

The mean diameters (obtained for the intermediate contribution in the fitting) of **1** and **2** as a function of the molar concentration of added tetraethylammonium perchlorate (TEAP) are shown in parts a and b of Figure 3, respectively. Because of technical problems (e.g., strong extinction coefficients in the visible which makes compulsory the use of very dilute samples that produce low scattering signals), we cannot obtain reliable data on the polydispersity of the samples. A size of about 100 nm is obtained for the species in acetonitrile solution in the absence of added salt for both **1** and **2**. This mean value is noticeably large when compared to the dimension calculated by CPK models for the cationic decametallic species (diameter, ~30 Å) and indicates the presence of aggregates of tens of supermolecules. The size of the aggregates grows with salt concentration, and for 0.01 M salt concentration it abruptly increases to micrometer dimensions. In Figure 3 the various symbols correspond to calculated radii for experimental measurements made at different scattering angles; for small aggregates, closed values are obtained for size (and for D) corresponding to translational diffusion motion. When the dimension of the aggregates increase (i.e., for added salt), a dependence of ϱ (and, as a consequence, on D) on $\mathbf{q}$ is connected with the contribution of internal motions of the particles superimposed on the translational diffusion motions. The same effect has been also observed in a similar system.[10] Experiments performed in other solvents, including water, gave qualitatively similar results, but their quantitative determination was not possible under our experimental conditions because of the poor quality of the results from very dilute water solutions (various optical impurities, such as bubbles and dust, cannot be easily removed from water) and because in nonpolar solvents such as benzene, toluene, and dichloromethane the dimension of the aggregates was in the micrometric scale even without salt addition.

2. Elastic Light Scattering. The light intensity I scattered by molecules in solution depends on the concentration c, the size and weight of dispersed molecules, and (for noninteracting molecules) the mass M. The Rayleigh ratio R_ϑ is given by

$$R_\vartheta = (I - I_s)R_0/I_0 = HcM \tag{3}$$

extrapolated at the zero angle limit. Here I_s and I_0 are the scattering of the solvent and the scattering of the reference sample, respectively, and R_0 is the Rayleigh ratio of the reference sample (usually benzene). H is the optical constant of the solution, defined as in eq 4.[11]

$$H = \frac{4\pi^2 n_0^2}{\lambda^4 N_a}\left(\frac{\partial n}{\partial c}\right)_T^2 \tag{4}$$

We performed measurements of I and I_s as a function of scattering angles for low concentrated samples at different ionic strength. The quantity measured is the excess scattering intensity $I_{ex} = (I - I_s)$ extrapolated at zero scattering angle. This quantity is proportional to the mass of the particles in the solution and gives indication about the presence of aggregates as inferred from eq 3.

The finite values for the excess scattering intensity calculated for **1** and **2** at low ionic strength cannot be explained by the presence of isolated molecules like "free" **1** and **2**. In fact, the excess intensity for molecules of 10 000 Da at 10^{-6} M concentration (10^{-5} g/mL) is nearly 10^{-3} times the scattering of pure benzene and, therefore, should not be detectable with our apparatus. A much larger structure is needed for reaching a detectable scattering signal. Because of the relatively weak signal, a quantitative analysis for the calculation of apparent molecular weight M is not possible; however, the excess intensity I_{ex} is, without doubt, indicative of the presence of large aggregates in solution. In Figure 4 we show the excess intensity as a function of salt concentration. It is possible to see a rapid variation of I_{ex} (i.e., of the apparent molecular weight as expressed by eq 3) as a function of salt concentration. It can be noted that such a rapid variation occurs at salt concentrations in which QELS detects micrometric aggregates (Figure 3). The results for high TEAP concentration (10^{-3} M) seem to deviate from the expected behavior. This behavior can be explained

---

(10) Engelhardt, Th.-P.; Belkoura, L.; Woermann, D.; Grimme, W. *Bernsen-Ges. Phys. Chem.* **1993**, *97*, 33.

(11) In *The Scattering of Light and Other Electromagnetic Radiation*; Kerker, M., Ed.; Academic Press: New York, 1969.

by considering that for very large aggregates most of the scattered light is in the small angle region, which is out of the experimental range for elastic light scattering. This problem does not affect dynamic light scattering results (Figure 3) because this technique is spectral and is independent of the absolute value of the scattered light intensity.[8]

The agreement between elastic and quasi-elastic light scattering data rules out the assignment of the diffusion coefficient at low ionic strength to the increase of friction factor due to the effect of electroviscosity.[12] In other words, the slow dynamics of our systems as revealed by quasi-elastic light scattering experiments is assigned to formation of aggregates.

B. Conductivity. Before discussion of conductivity experiments, some consideration has to be made. For the decametallic species **1** and **2**, conductivity values at very low concentrations are time-dependent. In fact, freshly prepared solutions exhibit conductivity values lower than aged solutions. This effect is particularly noticeable for the more dilute samples. The time-dependence of the conductivity can be rationalized by considering that **1** and **2** are nanometer-sized species; their solubility in fluid solution can take long times to occur. The time-dependence of the conductivity of the diluted concentrations is, therefore, probably due to slow solubilization. The fact that the conductivity values increase with time and asymptotically tend to the theoretical limiting value for a 1:20 electrolyte of ~30 Å diameter (as estimated from the mobility of the species) is in agreement with this explanation. At higher concentrations, the species are strongly associated (*vide infra*), and slow solubility no longer significatively affects the conductivity values. Because only aged solutions can be considered to be in thermodynamic equilibrium, the following discussion of the conductivities of **1** and **2** will be limited to the aged solutions.

Conductivity measurements in organic solvents have been extensively used to determine the structures of coordination compounds.[13,14] Equivalent conductivity, Λ_e, is expected to be linearly dependent on the square root of the equivalent concentration, $C_e^{1/2}$, if the nature of the conductant species remains unchanged.

For $[Ru(bpy)_3](PF_6)_2$, used as a reference, the equivalent conductivity changes linearly in the range of 2.5×10^{-6} to 5.0×10^{-4} M (5.0×10^{-6} to 1.0×10^{-3} N). At higher concentrations, however, Λ_e deviates markedly from linearity. This behavior can be attributed to ion-pair formation between $Ru(bpy)_3^{2+}$ and PF_6^- ions. The equivalent conductivity of the dilute solutions (5.0×10^{-6} to 1.0×10^{-4} N) of the decametallic species decreases drastically with concentration (Figure 5). However, for more concentrated solutions (1.0×10^{-4} to 8.0×10^{-3} N) equivalent conductivity is roughly constant with concentration.

Onsager's limiting law (Figure 5, inset), $\Lambda_0 - \Lambda_e = A\sqrt{C_e}$ (where Λ_0 and Λ_e are the equivalent conductivities at infinite dilution and at the concentration C_e, respectively),[13,14] expresses the linear decrement of the equivalent conductivity as a function of the square root of the concentration due to counterion shielding. The expected value of the slope is obtained for $Ru(bpy)_3^{2+}$ in the range of 2.5×10^{-6} to 5.0×10^{-4} M (5.0×10^{-6} to 1.0×10^{-3} N). The same equation, applied to the concentration range of 2.5×10^{-7} to 5.0×10^{-6} M (5.0×10^{-6} to 1.0×10^{-4} N) for **1** and **2**, gives slopes significantly different from the theoretical value of a 20:1 electrolyte. The failure of the law indicates that association processes are already effective for the studied supermolecules even at concentrations as low as 10^{-6} M.[15]

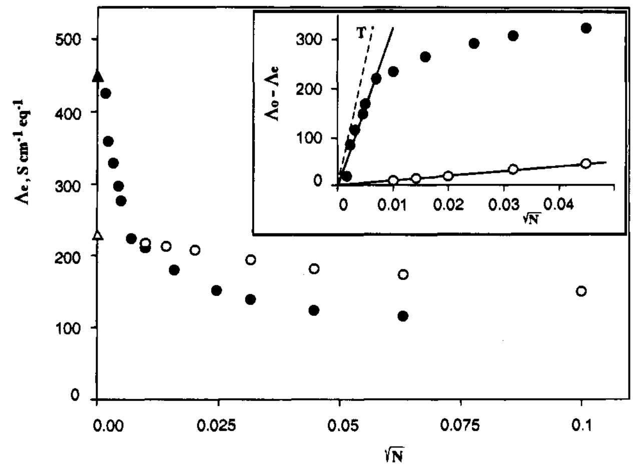

Figure 5. Equivalent conductivity (S cm^{-1} equiv^{-1}) vs square root of the equivalent concentration of **1** (solid circles) and $[Ru(bpy)_3](PF_6)_2$ (open circles) in acetonitrile. Inset: ($\Lambda_0 - \Lambda_e$) vs square root of the equivalent concentration The triangles are the theoretical limiting values of the equivalent conductivity for **1** and $[Ru(bpy)_3](PF_6)_2$. The solid lines are the initial slopes. The dashed line T in the inset is the theoretical slope of a 20:1 strong electrolyte calculated by using the Debye–Hückel–Onsager equation.

It is interesting to note that the equivalent conductivity of **1** at concentrations greater than 10^{-4} M is about 80% of the equivalent conductivity of the "free" hexafluorophosphate anion at infinite dilution (102 Ω^{-1} cm^{-1}), and when extrapolated to infinite dilution (if lower concentrations are not considered), it approximates PF_6^- equivalent conductivity. This is in agreement with our findings, where the hyperbranched decametallic cations are involved in larger edifices of presumably very low mobility.

Ion-pairing is the simplest act of aggregation of charged molecules so that the first association process occurring in the studied systems is certainly formation of solvent-stabilized ion-pairs. However, due to the nanometer dimension of the dendritic supermolecules and to the hydrophobic nature of their periphery, ion-pairing is probably only the first step of stronger and massive aggregation phenomena occurring in this family of compounds. Strong long-range attractive forces, which are known to occur for nanometer-sized systems (macromolecular solutions, particle dispersions, microemulsions, and so on),[16] can be sufficient to overcome the repulsive forces between the preformed supramolecular ion-pairs. The dimension of the aggregates measured by QELS definitively confirms this hypothesis. The main role of ion-pairing is, therefore, to transform the decanuclear species in "noncharged" supermolecules, decreasing electrostatic repulsion. This explanation is completely supported by the effect

---

(12) In *An Introduction to Dynamic Light Scattering by Macromolecules*; Schmitz, K. S., Ed.; Academic Press: New York, 1990.

(13) (a) Debye, P.; Hückel, E. *Phys. Z.* **1923**, *24*, 311. (b) Onsager, L. *Phys. Z.* **1926**, *27*, 388. (c) Feltham, R. D.; Hayter, R. G. *J. Chem. Soc.* **1964**, 4587. (d) Boggess, R. K.; Zatko, D. A. *J. Chem. Educ.* **1975**, *52*, 649.

(14) (a) Weaver, T. R.; Meyer, T. J.; Adeyemi, S. A.; Brown, G. M.; Eckberg, R. P.; Hatfield, W. E.; Johnson, E. C.; Murray, R. W.; Untereker, D. *J. Am. Chem. Soc.* **1975**, *97*, 3039. (b) Rillema, D. P.; Callahan, R. W.; Mack, K. B. *Inorg. Chem.* **1982**, *21*, 2589. (c) Bignozzi, C. A.; Roffia, S.; Chiorboli, C.; Davila, J.; Indelli, M. T.; Scandola, F. *Inorg. Chem.* **1989**, *28*, 4350.

(15) One can note that Λ_0 for **1**, calculated by a best fitting procedure of the equation developed by Debye, Hückel, and Onsager for strong electrolytes, is affected by strong uncertainty, and Onsager limiting law is hardly used. We would like to point out that, although the crude values are to be taken with care, the experimental slope is noticeably different from the theoretical value, even accounting for experimental uncertainty.

(16) (a) Derjaguin, B. V.; Landau, L. *Acta Phys. Chim. Debricina* **1941**, *14*, 633. (b) Verwey, E. J.; Overbeek, J. Th. G. *Theory of the Stability of Lyophobic Colloids*; Elsevier: Amsterdam, 1948.

of the added salt on the light scattering measurements. The solvent would play an important role in stabilizing (or destabilizing) ion-pair formation. In fact, nonpolar solvents such as dichloromethane and benzene lead to larger aggregates at low concentrations, most likely a consequence of stronger stabilization of ion-pairs.

Conclusion

The investigations reported here (based on laser light scattering and conductivity experiments) strongly indicate the occurrence of *aggregation phenomena for 1 and 2 at room temperature in fluid solution at very low concentrations*, and that, as a consequence, the nanometer-sized hyperbranched supermolecules investigated can be considered colloidal systems as far as aggregation properties are concerned. Attractive forces between the hydrophobic supermolecules are probably the basis for the production of huge, stabilized aggregates.[17-20]

It should be considered that, as previously noted, aggregation phenomena are usual for nanometer-sized compounds (e.g., proteins, chlorophylls, latex particles, microemulsions) and have been reported for many systems, including synthetically prepared hyperbranched molecules that are structurally similar to the present species.[10] These reported examples concern nonionic species with aggregation occurring at relatively high concentrations and/or with aggregation formed by a few single molecules. The case reported here is a profoundly different one: the species are (highly-charged) ionic ones, aggregation occurs at very low concentrations (lower than 10^{-6} M), and it concerns tens of "single" supermolecules. The results suggest new perspectives in the research field of luminescent and redox-active Ru(II) and Os(II) polynuclear compounds. For example, intriguing consequences on the interpretation of photophysical and electrochemical properties of such species could come from aggregation studies. In particular, the interpretation of photophysical properties of highly-charged polynuclear compounds could be improved by taking into account the possibility of intermolecular effects due to aggregation. Work in this direction is in progress in our laboratories.

Acknowledgment. We thank Professor V. Balzani for helpful suggestions and discussions. This work was supported by MURST, CNR, and NATO (Grant No. 920609). S.S. also acknowledges CNR for Grant No. 201.03.20.

JA9418518

---

(17) Attractive effects between hydrophobic aromatic moieties of large molecules are well-known[18] and are at the basis of recognition processes in natural[19] and "unnatural"[20] species.

(18) The literature on this topic is too vast to be exhaustively quoted. Representative examples can be found in the following: (a) *Inclusion Phenomena and Molecular Recognition*; Atwood, J. L., Ed.; Plenum: New York, 1990. (b) Vögtle, F. *Supramolecular Chemistry*; Wiley: Chichester, 1991. (c) *Supramolecular Chemistry* Balzani, V., De Cola, L., Eds.; Kluwer: Dordrecht, The Netherlands, 1992.

(19) See, for example: *Structure and Dynamics of Nucleic Acids, Proteins, and Membranes*; Clement, E., Chin, S., Eds.; Plenum: New York, 1986. (b) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, 2nd ed.; Wiley: New York, 1980.

(20) (a) Park, T. K.; Feng, Q.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1992**, *114*, 4529. (b) Diederich, F.; Dick, K. *J. Am. Chem. Soc.* **1984**, *106*, 8024. (c) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.