Spectroscopic Investigations of ADMA Encapsulated in Pyrogallol[4]arene Nanocapsules

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Pyrogallol[4]arenes form stable hydrogen-bonded nanocapsules that have unique properties that may make them suitable for diverse applications, such as catalysts and molecular transporters. Little is known about the behavior of the interior of these new materials in solution, and by using the solvent-dependent properties of 1-(9-anthryl)-3-(4-dimethylaniline) propane (ADMA), the inner phase properties of the hexamers are investigated. Steady-state and dynamic spectrofluorometric results are in agreement, are consistent with solid-state studies, and indicate that the majority of ADMA is sequestered in an extended conformation with the crystallization solvent. The conformational flexibility of ADMA is attributed to lower capsule occupancies (∼50%, i.e., 1 molecule per 2 capsules, one occupied and one empty) relative to our previous study with pyrene butyric acid (occupancy of 150%, i.e., 1.5 molecules per capsule) in which the probe was restricted within a nanocapsule. The nature of the encapsulated ADMA complexes are found to change with time, as there is either fluorophore leaching from the capsule or *endo-exo*-capsule solvent exchange. However, the choice of crystallizing solvent (ethyl acetate or acetonitrile) and PgC_n alkyl tail (C_6 or C_{10}) does not influence experimental outcomes. These research findings give a better understanding of the encapsulation versatility of these unique supramolecular assemblies and the protective nanopockets that can exist for guest molecules.

Introduction

Recognizing how many complex proteins and viruses self-assemble,[1] current research focuses on the analogous behavior of macromolecules in an effort to understand and imitate nature.[1−4] Self-assembling molecules utilize noncovalent interactions in order to form stable supramolecules.[5] One of the first examples of the formation of a voluminous nanocapsule was reported by Atwood et al.[5] In this study, six *C*-methylresorcin[4]arenes (CMRC, Figure 1) self-assemble with eight structural water molecules to form a nanocapsule with an internal volume of ∼1300 Å^3. This structure is held together by 60 hydrogen bonds and is stable in both polar and nonpolar environments.[5] The related *C*-alkylpyrogallol[4]arenes (general notation PgC_n, Figure 1) have been shown to form more stable hexameric nanocapsules in a number of studies.[5−10] Their enhanced stability, compared to their resorcin[4]arene[5] cousins, is attributed to the inclusion of an additional "upper rim" hydroxyl group, which results in a larger number of hydrogen-bonding interactions (72 total) and the exclusion of water molecules from the hydrogen-bonded capsule "seam".[6−8,11−17] The interior volume of the PgC_n nanocapsule is approximately 1250 Å^3, and the alkyl groups that radiate from the spheroidal assembly can range in length from ethyl to undecyl.[8]

Few reports have examined these new materials in solution to understand the nature of the host−guest interactions that facilitate their use in applications as diverse as catalysts, molecular transporters and sorters, and microreactors.[10,17−19] Recently, we encapsulated the fluorescent reporter pyrene butyric acid (PBA) in a PgC_6 nanocapsule (Figure 1) in order to obtain "inner-phase" information from the assembly.[17] X-ray crystallographic data showed that the nanocapsules were mostly doubly occupied by the guest, and in this case, the two fluorophores were well-separated by the presence of encapsulated solvent and the butyric acid side chains. Spectroscopic and crystallographic investigations determined that PBA interacted with the walls of the capsule in both solution and the solid state. The presence of the solvent (acetonitrile, ACN) encapsulated with PBA was confirmed in solution by the addition of a fluorescent quencher, *N*,*N*-dimethylaniline (DMA). For example, the addition of DMA to free PBA dissolved in tetrahydrofuran (THF) showed exciplex emission due to charge transfer (CT) at ca. 440 nm. However, PBA−DMA exciplex emission is well-documented to be absent in the presence of ACN.[17,20,21] In our experiments, this lack of emission from encapsulated PBA confirmed the presence of ACN in the PBA−PgC_6 complexes.

Like PBA in the presence of DMA, 1-(9-anthryl)-3-(4-dimethylaniline) propane (ADMA, Figure 1) also forms a CT complex between fluorophore and quencher. However, this molecule contains both a fluorescent moiety, anthracene (acceptor, A), and a quenching unit, dimethylaniline (donor, D), which are connected by a propyl linker. Therefore, ADMA can undergo intramolecular CT when irradiated by accepting an electron from the DMA fragment. Moreover, the ADMA molecule can fold to form a sandwich-like arrangement with π stacking between DMA and the polyaromatic unit.[22] The ADMA molecule is an example of a D−$(CH_2)_n$−A system. In such D−A systems, CT is diffusion controlled. In the case of ADMA, diffusion can be restricted by many factors, including solvent viscosity or polarity and steric constraints that keep the donor and acceptor apart.[23−25] Hence, ADMA has been extensively

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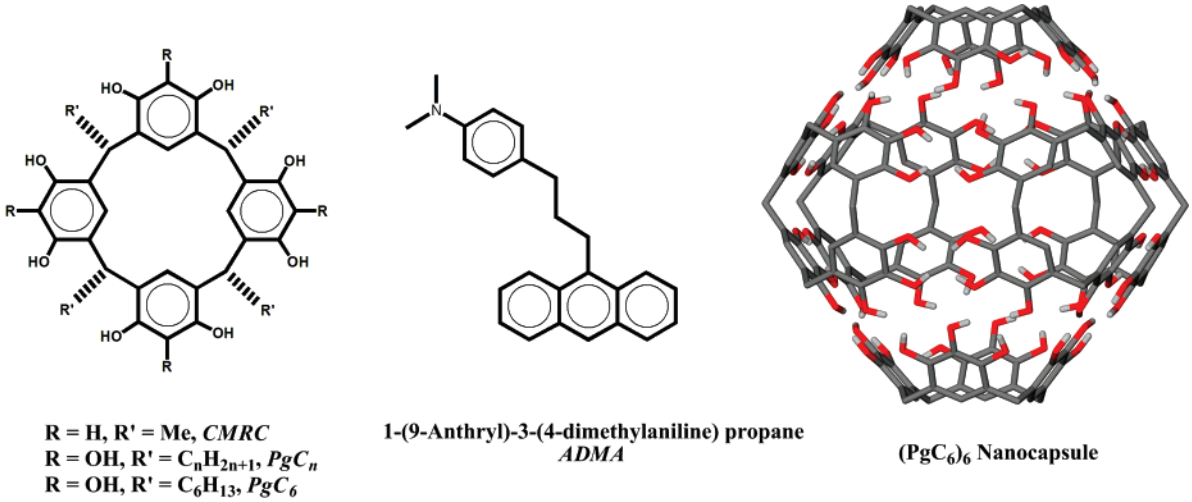

Figure 1. Molecular structure of CMRC, ADMA, and PgC_6 nanocapsule (C_6 groups are not shown in the PgC_6 framework for clarity purposes).

studied in solvents with a wide range dielectric constants (ϵ), such as ethyl acetate (EA, $\epsilon = 6.02$), THF ($\epsilon = 8.05$), and ACN ($\epsilon = 37.5$), which are all pertinent to this report.[25−31] Like the PBA−DMA system, CT in ADMA results in intense exciplex emission (ca. 540 nm) in solvents such as EA and THF, but not ACN due its high dielectric constant.[30]

To date, ADMA and its derivatives[32] have been used to study solvation and reactivity in complex media, such as supercritical fluids,[27,33] micelles,[34] and polymers.[32] Herein, we report the encapsulation of ADMA in both PgC_6 and PgC_{10} hexamers in the presence of either ACN (PgC_6) or EA (PgC_6 and PgC_{10}). Nanocapsule crystals, containing ADMA and EA or ACN, were dissolved and studied in THF due to the strong exciplex emission resulting from the CT.[28] This study differs markedly from the PBA work, where the DMA quencher was added to a solution containing the host−guest assembly.[17] The PgC_n host capsules should accommodate an ADMA guest molecule, with a molecular volume of ~347 Å^3.[35] It is anticipated that ADMA will adjust its spatial conformation in response to the potential host−guest interactions with the hexameric assembly.

Experimental Section

Materials. All solvents were obtained in the purest commercially available form, used as received, and are as follows: HPLC-grade ACN, EA, and THF (Fisher Scientific, Fair Lawn, New Jersey). *C*-alkylpyrogallol[4]arenes[8,36] and ADMA[37] were synthesized according to literature procedures.

Assembly of the supramolecular complexes was facilitated by sonication of a saturated solution of PgC_n and ADMA in either ACN or EA.[38] As previously reported, the composition of the crystals (i.e., confirmation of the presence of spheroids) was characterized by single-crystal X-ray diffraction and ^{1}H NMR spectroscopy, the latter of which determined the percentage of probe relative to PgC_6 within the crystals.[38]

Stock solutions (~10^{-3} M ADMA) of the fluorophore or the complex were prepared by dissolving the dye or a single crystal of the latter in the appropriate solvent. To further confirm probe occupation within the nanocapsules, crystals were irradiated at 365 nm with a UV lamp to observe the ADMA fluorescence. Diluted samples were prepared by quantitatively transferring known aliquots of the stock solutions into volumetric flasks and diluting to volume. The final concentration of ADMA in any solvent system was optically dilute (~10^{-6} M). Samples were examined immediately upon mixing, with the exception of the time-lapse studies that were stored in the dark in sealed vials, and were interrogated at room temperature (20−25 °C).

UV/Vis Absorption Measurements. All spectra were collected in 1 cm^2 Suprasil quartz cuvettes, and absorption spectra were recorded on a Hitachi U-3000 double-beam spectrophotometer (Danbury, CT) with a scan rate of 120 nm/min and a slit width of 1 nm. Spectra were blank corrected for the possible absorption of solvent and the nanocapsules in solution.

Fluorescence Emission Measurements. Spectra were measured with a Varian Cary Eclipse fluorometer (Palo Alto, CA). The excitation source was a 15 W xenon arc lamp, pulsed at 80 Hz. Samples were excited at 369 nm, and the emission was collected from 370−700 nm at 2 nm steps, with a slit width of 5 nm. The scan rate was 120 nm/min, and the averaging time was 0.5 s. All emission spectra were blank and absorbance corrected.

Fluorescence Lifetime Measurements. Lifetimes were collected in the frequency domain,[39,40] on a SLM 48000 DSCF/MHF spectrofluorometer, with multiharmonic, Fourier transform phase-modulation capabilities. The excitation source was a Coherent Innova 307C argon ion laser (Santa Clara, CA) operated at 351 nm and 250 mW. In MHF mode, however, only a small fraction of the excitation power interrogated the sample. A base frequency of 4.0 MHz and a cross-correlation frequency of 7.000 Hz were used; 10 pairs of sample−reference measurements were collected in triplicate for each sample, and each measurement contained 50 internal averages. The lifetime reference ($\tau_{ref} = 1.34$ ns) was POPOP, 1,4-bis[5-phenyl-2-oxazolyl]benzene, (Sigma, St. Louis, MO) in ethanol. The following filters were employed for emission collection: a 370 long-pass (KV-370 Schott Glass Technologies, Duryea, PA)/610 short-pass (03 SWP 610 Melles Griot, Irvine, CA) filter combination, a 400 nm (80 nm band-pass, 03 FIB 002 Melles Griot), a 550 nm (40 nm band-pass, 03 FIV 044 Melles Griot), a 420 nm (10 nm band-pass, P10−420-F-Q920 Corion CVI Laser Corporation, Albuquerque, NM), and a 540 nm (10 nm band-pass, P10−540-F-986P Corion CVI). Lifetime data were analyzed by a self-modeling maximum entropy method (MEM) commercial software package (Phase5, Maximum Entropy Data Consultants, Cambridge, U.K.),[41−43] and results were compared to those obtained from a standard nonlinear least-squares (NLLS) software program (Globals Unlimited, Laboratory for Fluorescence Dynamics, Urbana−Champaign, IL). Three replicates for each sample were analyzed with Phase5, as both individual and combined files, using a lifetime window contain-

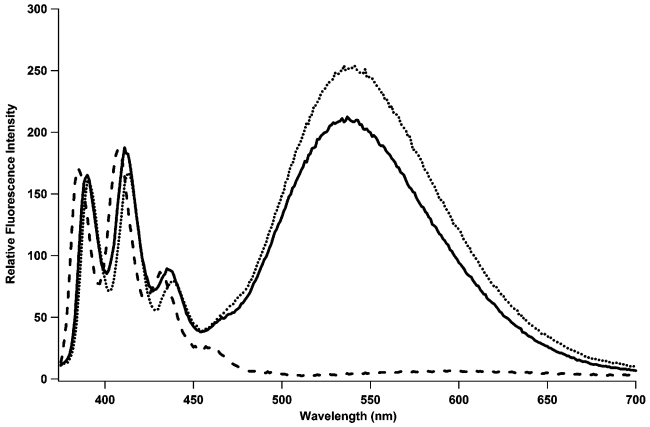

Figure 2. Fluorescence emission spectra of free ADMA in THF (· · ·), ethyl acetate (—), and acetonitrile (— — —).

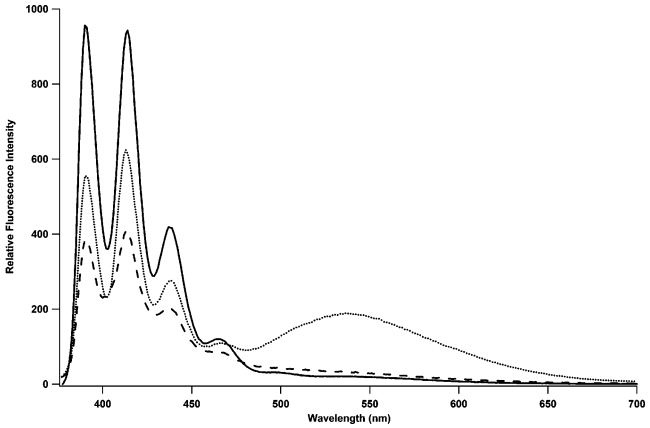

Figure 3. Fluorescence emission spectra of the ADMA−EA−PgC_6 complex in THF (— — —) and the ADMA−ACN−PgC_6 complex in THF on day 1 (—) and day 12 (· · ·).

ing 500 discrete, equally spaced cells from 0.01 to 50 ns. The three individual replicates and a linked file were also analyzed with Globals.

Results and Discussion

Single-crystal X-ray diffraction and ^{1}H NMR spectroscopy[38] revealed PgC_6 nanocapsules that have an overall population of ~50% (i.e., 1 molecules per 2 capsules, one occupied and one empty) and are likely to be monopopulated. This is substantially lower than the PBA occupancy of 150% (i.e., 1.5 molecules per capsule) even though the crystal unit cell dimensions closely match those found for PBA-containing nanocapsules, with an interior volume of ~1250 Å^3.[17] In the case of ADMA, lower nanocapsule occupancy may be attributable to its conformational flexibility, as it has the ability to adopt conformations ranging from folded (sandwich-like arrangement of aromatic moieties) to fully extended (noninteracting aromatic moieties).[22,23−25]

Steady-state fluorescence emission measurements determine the overall or average spectral properties of a sample, whereas, dynamic fluorescence lifetime techniques are frequently used to enhance steady-state measurements, providing more detailed information through the additional discriminating factor.[21,44] Given the complex nature of the PgC_6 supramolecular assemblies, both fluorescence emission spectra and lifetimes were measured. Results from these solution studies are shown in Figures 2−4 and Table 1. As suggested in the literature,[44] both NLLS and MEM lifetime analyses were performed. Lifetimes recovered from both methods were found to be in very good agreement. Table 1 shows representative fluorescence lifetimes

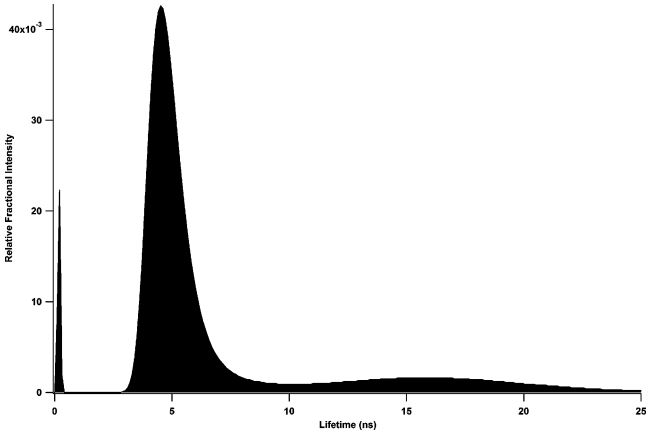

Figure 4. Representative MEM plot of the fluorescence lifetime distribution recovered for the ADMA−ACN−PgC_6 complex dissolved in THF.

TABLE 1: Representative Fluorescence Lifetimes (τ) and Fractional Intensities (α) of ADMA Recovered Using NLLS Analysis[a]

sample	τ_1	(α_1)	τ_2	(α_2)	τ_3	(α_3)	χ^2
ADMA in ACN	0.00	(0.33)	6.48	(0.67)			1.4
ADMA in EA	0.08	(0.14)	4.31	(0.21)	13.32	(0.65)	2.3
ADMA in THF	0.00	(0.079)	4.33	(0.18)	16.96	(0.74)	3.9
ADMA−ACN−PgC_6 complex in THF	0.17	(0.033)	4.67	(0.76)	14.69	(0.21)	1.1

[a] Using the 370−610 nm filter combination.

(τ) and fractional intensity contributions (α) recovered by NLLS analysis for ADMA in different media.[41] A representative MEM plot is also shown in Figure 4 to illustrate the distributed nature of the recovered lifetime components. Total lifetime distribution analysis (TLDA), using a broad filter window, was also performed. In addition, broad (80 or 40 nm) and narrow (10 nm) band-pass filters that were centered at the spectral features of interest—anthracene moiety emission at ca. 400 nm and the exciplex emission at ca. 540 nm—were included in the study.

Free ADMA. Figure 2 shows the fluorescence emission spectra of free ADMA in neat solvents. In agreement with the literature,[28,29] ADMA exciplex emission in THF and EA is distinct, a broad, featureless band at 540 nm. In ACN, exciplex emission is not easily discernible, but there is a very weak broad emission band centered around 580 nm. This observation is also consistent with the ADMA and DMA literature, where exciplex emission, if noted, is red shifted (580 vs 540 nm) due to an increase in the microenvironmental polarity of ACN, relative to THF or EA.[17,20,28,45] Also consistent with published reports[26,27,29,31,46,47] is the recovery of two definitive lifetime components (τ_2 and τ_3) in Table 1 that are attributable to ADMA. The τ_2 contribution (ca. 4 ns in THF and EA) is due to the decay of the anthracene moiety. A similar lifetime was recovered for ADMA in ACN, where only one lifetime was recovered.[28,30] Comparable lifetime results were observed in mineral oil, where exciplex emission is minimized due to the high solvent viscosity (μ = 0.02310 Pa·s), which prevents ADMA folding. In addition, the lifetime of anthracene, the parent compound, was measured in THF and is 3.92 ns. The τ_3 lifetime (ca. 15 ns) is attributed to the exciplex decay. These lifetime assignments were confirmed by isolating specific spectral regions with band-pass filters, as described previously. The shortest lifetime component, τ_1, as observed in both samples and blanks, was noted in previous studies[48−50] and is attributed to scatter and instrumental artifact.[42,43] In addition, in polar

solvents ($\epsilon > 5.4$), ADMA is reported to have biexponential decay,[29,46] including a picosecond lifetime component. Given the frequency range of the instrument, this component is irresolvable and may contribute to the larger fractional intensity ($\alpha \approx 0.3$) assigned to τ_1 of free ADMA in ACN.

In general, the fluorescence lifetime data and steady-state emission spectral profiles agree. In THF and EA, the exciplex emission of free ADMA is prominent in both the spectra (Figure 2) and the lifetime distribution ($\alpha \approx 0.7$ for τ_3, Table 1). Despite there being occasional evidence of very weak exciplex formation in the emission spectrum for ADMA in ACN,[23,30] no lifetime attributable to exciplex emission was recovered, consistent with the literature.[17,20,26−29,31,45−47]

Encapsulated ADMA. Figure 3 shows fluorescence emission spectra of ADMA−PgC_6 complexes that were crystallized with EA or ACN. In all cases, the spectra of the ADMA−PgC_n complexes (PgC_{10}, not shown) show little, if any, exciplex emission. However, the lifetime distribution of the ADMA−ACN−PgC_6 complex does reveal the presence of a minor amount of exciplex emission ($\alpha \approx 0.2$ for τ_3). Similar results were obtained for both ADMA−EA−PgC_6 and −PgC_{10} capsules. These data clearly indicate that the vast majority of ADMA is encapsulated, as *exo*-capsule ADMA (ADMA residing exterior to the nanocapsule in the bulk solvent) will result in a substantial exciplex emission, not noted to any appreciable extent in the fluorescence emission spectra or lifetimes. Control studies were performed to confirm that the lack of exciplex emission (indicating encapsulation) is not an artifact from the minuscule amounts of ACN (suppresses exciplex emission) potentially leaching from the nanocapsules. The addition of a relatively large amount ($\sim$100 μL) of ACN to free ADMA ($\sim 10^{-6}$ M) in THF (2500 μL) did not affect the photophysics of ADMA (i.e., ADMA exciplex emission remains very pronounced and nearly unchanged). Moreover, compared to free ADMA, the fluorescence emission intensity of *endo*-ADMA (ADMA residing inside the nanocapsule) was significantly enhanced (2-fold when encapsulated with EA and 5-fold with ACN). This enhancement is expected for a fluorophore that is retained and/or constrained in a protective microenvironment and is also not an artifact, as all emission spectra are absorbance and blank corrected. Control experiments, where ADMA was added to preformed nanocapsules, gave the same results as those for free ADMA. For the ADMA−PgC_6 capsules containing ACN, the emission intensity was similar to free ADMA in highly viscous mineral oil.[26]

The steady-state data and lifetime results indicate that the encapsulated ADMA is most likely in an extended conformation. For example, it is known that exciplex emission from free ADMA in EA results from a folded ADMA conformation,[29,30] and such emission is not seen for the ADMA−EA−PgC_6 complex. In the case where ACN is the solvent, non-emissive CT from free ADMA is energetically more favorable from the extended conformation.[26,30] It is the folded conformation that occasionally leads to CT emission being observed.[26,30] The ADMA−ACN−PgC_6 lifetime measurements show a minor amount of exciplex emission, indicating that some population of the ADMA may be in a folded conformation either *endo*- or *exo*-capsule. The extremely small exciplex contribution seen in the emission spectra supports the *endo*-capsule model, as exciplex emission in THF (*exo*-capsule) would be rather pronounced. The general lack of exciplex emission from the ADMA−PgC_n complexes indicates that the majority of the *endo*-ADMA is trapped in the supramolecular assembly in a manner that does not favor folding.

The stability of the complex was also examined. In Figure 3, the intensity of the exciplex emission from the ADMA−ACN−PgC_6 complex is shown to change significantly (10% to 44%) after 12 days. This result indicates that ADMA leaches out of the capsules into the surrounding THF, where it adopts the expected folded conformation that results in exciplex emission. The possibilities of either THF leaching into the capsule or ADMA folding while inside cannot be ruled out. However, given the environmental limitations of the capsule and the fact that this observation was only made after significant passage of time, this explanation is unlikely. Similar results were not obtained for time-lapse studies of ADMA−EA−PgC_6 complexes. The emission intensity due to the anthracene moiety decreased without the excepted increase in the exciplex spectral region (ca. 540 nm), as seen with ADMA−ACN−PgP_6. Further investigation of free ADMA in EA also indicated anomalous behavior over time; therefore, additional studies of the photophysics of ADMA in EA are being carried out.

Conclusions

Solution and solid-state results[38] agree and indicate that ADMA and the crystallization solvents (EA or ACN) are retained in the PgC_6 and PgC_{10} nanocapsules, with the encapsulated ADMA in the more energetically favorable extended conformation.[51,52] Similar results were reported by Güsten et al. for an ADMA-like molecule in polymeric matrices, where the restricted internal rotation of ADMA prevented the formation of the sandwich conformation and exciplex emission.[53] It is clear from the spectral data that the nanocapsule provides a protective microenvironment for the ADMA guest molecule. However, the conformational flexibility of this probe compared to PBA appears to hinder the ease of encapsulation (lower occupancy), as well as the robustness (extent of leaching) of this supramolecular assembly.[38] The crystallizing solvent (ACN vs EA) and the nanocapsule alkyl tail length (C_6 vs C_{10}) appear to have little effect on the creation and overall nature of these assemblies. These research findings guide our future studies with other reporter molecules with the intent of gaining a better understanding of the versatility of these unique supramolecular assemblies and of directing future synthesis to harness their chemical and physical properties for specific applications.

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