

Forum K Polymer Materials

K01 (Invited)

Modification of PVDF/ATP Hybrid Membrane for Adsorption of Cd(II) from Aqueous Solution and Improving Antifouling Properties

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Poly(vinylidene fluoride) /attapulgitite (PVDF/ATP) hybrid membrane was prepared as the sorbent for adsorption of heavy metal ions Cd(II) from aqueous solution. To improve hydrophilicity and anti-fouling properties of the hybrid membrane, sulfobetaine-based zwitterionic monomer 3-(methacryloylamino) propyl-dimethyl- (3-sulfopropyl) ammonium hydroxide (MPDSAHA) was grafted on the PVDF/ATP membrane surface via radical polymerization. The structures and surface characteristics of the (PVDF/ATP)-g-MPDSAHA hybrid membrane were investigated by Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM), respectively. The adsorption of Cd(II) ions on the hybrid membrane was studied in batch experiments and it was found that the surface modification could obviously increase the adsorption capacity for Cd(II) ions. The adsorption kinetics of the hybrid membrane fitted a pseudo-second-order kinetic model. The results indicated that chemisorption processes could be the rate-limiting steps in the process of Cd(II) ions adsorption. The improvement of hydrophilicity and adsorption of Cd(II) ions, the decrease of Lysozyme (Lys-z) deposited on the membrane were resulted from the high coverage of MPDSAHA gel layer on the PVDF membrane surface.

K02 (Invited)

Optimization for Saponification of BLPAS by Response Surface Methodology

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The saponification hydrolysis of adsorbent composites comprising of bentonite/sodium lignosulfonate graft-polymerized with acrylamide and 2-acrylamido-2-methylpropanesulfonic

acid (BLPAS) was investigated by response surface methodology. In the process, the concentration of NaOH, saponification temperature and saponification time were used as response variables and the adsorption capacity of lead ions and the selective coefficient of lead to copper ions were used as response values to establish the Box-Behnken model. The optimum saponification conditions were obtained as follows: the concentration of NaOH is 1.85mol/L, the saponification temperature is 81 °C, the saponification time is 1.75 h. The adsorption properties of BLPAS were significantly improved by saponification and the adsorption capacities of the saponified BLPAS (BLPAS-S) for Pb²⁺ and Cu²⁺ in Pb(NO₃)₂/Cu(NO₃)₂ binary metal ion solution are 1.225, 1.047 mmol/g, respectively, and the selective coefficient of Pb²⁺ to Cu²⁺ is 2.623. EA, FTIR and XPS characterizations indicated that there were –CONH₂, –COONa and –SO₃Na groups in the structure of BLPAS-S.

Keywords: lignin; adsorbent; saponification; selective adsorption; response surface methodology

K03

Progress in Carboxyl-Functionalized Poly(arylene ether nitrile)s and Their Functional Composites

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Poly(arylene ether nitrile)s (PENs), as a new class of high performance thermoplastic special engineering plastics, possess high heat-resistance, high mechanical strength, good chemical-resistance, excellent creep-resistance and flame-resistance, etc., and have broad application prospects in the aerospace, rail transportation, automobile manufacturing, machinery industry and many other fields. However, many studies have shown that PENs have high melting temperatures due to the aromatic rigid structures, and are almost insoluble in common organic solvents. These problems limit the synthesis, processing and applications of PENs. In this work, a twist and non-coplanar phenolphthalin moiety with pendant carboxyl groups was successfully introduced into the polymer main chain, and a series of novel carboxyl-functionalized poly(arylene ether nitrile)s (CPENs) were synthesized. The relationship between the structure and properties of CPENs was systemically studied. It was found that the CPENs are special polymers with a set of high-performance engineering plastic, fluorescent functional polymer and reactive polymer. Then, by taking advantage of the chemical reactivity of the carboxyl functional groups, CPEN fluorescence and dielectric functional composites were developed. First, CPEN fluorescent composites were prepared by a rare-earth-doping method and rare-earth-ions coordination

method, respectively. The fluorescence colors of CPEN fluorescent composites are well controllable by adjusting the ratio of rare-earth ions. Then, CPEN was used as a novel polymeric surface grafting agent, and barium titanate (BT) nanoparticles were successfully surface grafted with CPEN via a rotary coating technology combining with a heat-treatment bonding process. By using CPEN-grafted-BT as nanofillers, PEN-based nanocomposites with high dielectric constant, low dielectric loss and excellent mechanical properties were prepared.

Keywords: Poly(arylene ether nitrile)s, carboxyl-functionalization, functional composites, fluorescence, dielectric properties.

K04

Synthesis and Properties of N-Polyaryleneindole Ether

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Series of N-Polyaryleneindole ether were facile synthesized via a catalyst-free nucleophilic substitution reaction. The resulting polymers enjoy high glass transition temperatures ($T_g \geq 191$ °C) and good thermal stability with high decomposition temperature ($T_5\% \geq 492$ °C).

Keywords: N-Polyaryleneindole ether, High-performance polymer, Glass transition temperature

K05

Preparation of Functionalized Carbon Nanotube based on Friedel-Crafts reaction and Its Reinforced Polymer Composite fibers

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Polymer fiber with high strength and high modulus has been an important topic in the fiber industry, and carbon nano-material reinforced polymer fiber is one of the hot spots in the research field. However, it is particularly the challenge to ensure that carbon nano-materials homogeneously disperse in the polymer. In this paper, multi-wall carbon nanotubes (MWCNTs)

were functionalized through grafting polymer chains to their surface by Friedel-Crafts reaction and then blended the functionalized MWCNTs (f-MWCNTs) with the polymer. The blend solution was wet-spun to prepare f-MWCNTs reinforced polymer composite fibers. The results show that f-MWCNTs are kept higher integrity after Friedel-Crafts treatment than carbon nanotubes treated by traditional acidification process. A low content of f-MWCNTs causes a substantial increase of the strength and modulus for the composite fibers, and with the increase of the content of the nanotubes the mechanical properties of the fibers improve continuously. But when the content reaches a certain value, the strength of fibers decreases, which is likely caused by agglomeration of the carbon nanotubes to some extent.

Keywords: Polymer, Carbon Nanotube, Dispersion, Composite fibers

K06

Synthesis and Evaluation of a New Kind of Kinetic Hydrate Inhibitor

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A new kind of kinetic hydrate inhibitor (KHI) named KL-1 as the ramification of poly(*N*-vinyl caprolactam) (PVCap), was synthesized successfully using of precipitation polymerization of two monomers containing C=C. The hydrate inhibition performance of KL-1 was assessed in a high pressure sapphire cell, and the induction time of hydrate formation was determined by the visual observation method and compared with several commercial KHIs such as Inhibex 501 and VC-713. Meanwhile, the compatibility between KL-1 newly developed and corrosion inhibitor was also studied in this work. The experimental results show that KL-1 is superior to Inhibex 501 and VC-713 mentioned above, and can show longer induction time for appearance of hydrate crystals at the same subcooling condition. Additionally, based on the measurement of inhibition time, we found that the maximum tolerated subcooling of KL-1 does not always increase with the increase of dosage, and the most suitable dosage was determined to 1.0 wt% or so. Finally, we also demonstrated that KL-1 has well compatibility with corrosion inhibitor, and ethanol can be used as synergist to improve the performance of KL-1 remarkably.

Keywords: kinetic hydrate inhibitor, induction time, maximum tolerated subcooling, inhibition performance

K07 (Invited)

How to Form Surface Wrinkles on Inorganic Substrates?

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The micro structure regulation based on the surface of polymer matrix is a major research topic in the field of nano science, especially the construction and regulation of the bionic structure on the surface of the elastomer. A mini review is discussed based on the classification of layered system, gradient film and homogeneous film. In addition to the fabrication of typical wrinkles, a few outstanding works on the generation and application of reversible wrinkles, hierarchical wrinkles and three dimensional wrinkles are highlighted. Generally surface wrinkles are formed on a soft material with a hard skin. But up to date, it is hard to find surface wrinkles formed on a hard inorganic material with a hard skin. How to form surface wrinkles on inorganic substrates? Here we demonstrate an original route to realize this. Firstly, surface wrinkles are formed on soft materials as the common method, then the soft materials with surface wrinkles are transformed into inorganic substrate through to a polymer-to-inorganic conversion.

Keywords Surface wrinkle; Surface instability; Polymer precursor

K08

Plavis Introduction (Polyimide)

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Plavis™ polyimide shapes provide superior high-temperature resistance, excellent wear and friction properties, good electrical and physical properties, and chemical inertness.

Plavis™ polyimide delivers outstanding resistance to creep and lubricated or unlubricated performance, ultra-low outgassing, excellent mechanical strength and impact resistance. PLAVIS polyimide is applied in the industries of aircraft and aerospace, automotive, electrical and electronics, chemical and mechanical engineering, semiconductors, etc.

Plavis™ polyimide can be applied to the products included Rotary seal rings , Thrust

washers and discs ,Bushings ,Flanged bearings • Plungers • Printer wire guides • Spline couplings
• Wear strips • Valve seats • Thermal and electrical insulators • Wafer clamping, polishing and grinding rings • Wafer guides & carriers • Vacuum pads • Die pickup collets

Keywords: • High-temperature performance. • Wear-Resistance • Chemical Resistance • Easy to Machine • Good Electrical Properties - Insulative • Creep Resistant • Radiation Resistance • Ultra Low Outgassing • Isostatically molded for uniform multidirectional performance.

K09

Preparation and Electrooptical Performance Research of Functional Europium Complexes

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To aim at these key problems of europium complexes, such as low quantum efficiency, Eu-based polymer PLEDs very little and electroluminescence properties not very good, fluorescent lifetime of amounts of sensors is very short and these sensors almost used in organic solvents, and so on. A series of trinuclear europium complexes, highly electroluminescent properties Eu-based polymers PLEDs, and anions sensor with long fluorescent lifetime as well as can be used in pure water have been successfully prepared. PL result showed the quantum efficiency of trinuclear europium complexes was higher about 30% than that of corresponding mononuclear europium complex, respectively. These results indicated that the introduction of ligands with multiple binding sites in europium complex could effectively increase the quantum efficiency of europium complexes. Meanwhile, this is first report the EL performance of Eu-complexes based on tpy as neutral ligands. Our results demonstrate the potential application of polymerizable tpy ligands in high performance EL europium-complex polymers. Lastly, to obtain the anion sensor, which can be used in pure water, we fabricated a novel Eu-based fluorescent hydrogel probe using Eu(TTA)₂vinyl-phen and NIPAAm as monomers by free radical copolymerization, the emission spectra titration results showed this Eu-based hydrogel has good selective and sensitive ability for H₂PO₄⁻ in pure water, the detection limit is 1×10⁻⁵ M.

Keywords: Trinuclear europium complex, PLEDs, Eu-based polymer, Tpy, anions sensor, Fluorescent hydrogel

K10

High-Performance PVAc-Based Core/Shell Composite Emulsion: Preparation, Morphology and Properties

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Based on the practical problems of the poly(vinyl acetate) emulsion in application, i.e. the poor water- and heat- resistance and the poor low temperature resistant and so on, a novel design idea was proposed for fabricating one-component and high-performance poly(vinyl acetate)-based core/shell emulsions by the grafting and grafting-copolymerization. The theory of particle design was used as the basis to fabricate the core/shell structural composite emulsion with vinyl acetate polymer as core, the polymer of hydrophobic monomer as shell. The poly(vinyl acetate)-based core-shell composite emulsions with various morphologies were synthesized via the technique of "starved feeding" and semi-continuous seeded emulsion polymerization. The effect of react conditions on morphologies and structures of the products, such as core/shell ratio, the content of grafting/copolymerization monomer etc. was thoroughly investigated with the structural and morphological test means, including FTIR、DSC、DLS and micro morphology characterizations(SEM, TEM). The particle size of the prepared composite core/shell latex particles was about 250-330nm, and the particle morphology had obviously multiple evolution trend, in which there were three typical morphologies, strawberry type, semi-coated type and ball-type, respectively. The boiling water time of adhesive bonded sample was more than 180 minutes. The maximum values of adhesive dry strength and wet strength of the prepared composite emulsion were 10.4MPa and 2.7MPa, respectively. Based upon the experimental results, the possible formation mechanisms and morphological evolution mechanism of the prepared latex particles were discussed.

Keywords: Poly(vinyl acetate)-based composite emulsion; inverse core/shell structure; grafting/grafting-copolymerization; morphological evolution; adhesive performance.

K11

One-step Bimodel Grafting Via Multicomponent Reaction Toward Antifouling and Antibacterial TFC RO Membranes

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The simple methods for dual functional modification of membrane surface have been rarely reported but are highly desired for fabrication of antifouling and antibacterial membranes. In this work, we take advantage of a multicomponent reaction Ugi-4CR (Ugi four-component reaction) to prepare novel antifouling and antibacterial reverse osmosis (RO) membranes. With the aid of massive residual carboxyl groups on commercial polyamide RO membranes as the anchor and methyl isocyanate as one component, a hydrophilic macromolecular component aldehyded methoxy poly(ethylene glycol) (MPEG-CHO) and an amino-terminated antibacterial component, tris(2-aminoethyl)amine (TAEA) or sulfamethoxazole (SMZ) were grafted onto the surface in a single step via the Ugi-4CR. The surfaces of the original and modified membranes were characterized by ATR-FTIR, XPS, TG, WCA, FESEM and AFM measurements. The antifouling performance was evaluated by cross-flow filtration of protein and inorganic salt solution. The antibacterial performance was assessed by the shake flask method. The results show that the Ugi-4CR was successfully conducted on the RO membrane surface with MPEG-CHO and antibacterial agents successfully grafted. The surface roughness decreases and surface hydrophilicity improves upon modification. After 48 h fouling experiments, the obtained PA-g-PEG/TAEA and PA-g-PEG/SMZ membranes show obviously lower flux attenuation ratio and higher flux recovery ratio than the original membrane in both cases when fouled by protein or inorganic salt. In addition, the bacterial concentration in the suspension shook with modified membranes was much less than that of the original membrane. As for the PA-g-PEG/SMZ membrane, the bacteria growth was hardly seen even after 24 h culture. In contrast to current multi-step grafting processes, this work reports a “one pot procedure” with two functional groups grafted simultaneously under very mild condition without the use of catalyst.

Keywords: Multicomponent reaction; surface modification; RO membrane; antifouling ; antibacterial

K12

Molecular Chain Bonding Synthesis of Nanoporous, Flexible and Conductive Polymer Composite for Energy Storage

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The porous polymer composites is one of the most potential materials for the future, but it faces great challenges in constructing nanopores in polymer composite. In this work, molecular chain bonding of polymer is developed to synthesize flexible and conductive polymer composites. The design philosophy of molecular chain bonding, that the single polymer phase can be converted to two phases by molecular chain bonding of partial polymer chains, and then the soluble polymer phase is removed, would be popularized in constructing other porous polymer composites. The nanoporous polymer composite not only possesses a nanoporous structure, but also presents ultra-high mechanical properties (even comparable with that of classic structural materials) and fatigue resistance under deformation. It achieves 7 fold capacitance increase to that of nonporous composites. Furthermore, further applications are demonstrated as high-performance supercapacitor. The device exhibits ultra-stable charge-discharge cycle life under repeatedly bending (larger than 5000 cycles). The findings of the nanoporous polymer composite are supposed to enlighten a broad area of advanced porous polymer composites for flexible energy-storage devices.

K13

Application of a Photocatalytic Beads for Decomposition of Dye Molecules in a Photocatalytic Membrane Reactor Under Visible

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A novel catalytic bead was synthesized by surface modification of polystyrene (PS) beads. The PS beads were modified by photoinduced grafting of poly (1-(4-vinylbenzyl)-3-methylimidazolium chloride) (PVBMC) followed by loading with POM ($H_3PMo_{12}O_{40}$). We used them as catalysts to design a photocatalytic membrane reactor (PMR). The PMR was successfully used for degradation of dyes in water under visible light. The modified beads were characterized by TGA, FT-IR, FESEM and XPS. Acid orange 7 (AO7) was used as a model dye molecule to evaluate the photocatalytic performance of the PS-g-PVBMC-POM beads. The results indicate that the PVBMC-POM composites were successfully immobilized onto the surface of PS beads. The best performance of the PMR was obtained when the pH of AO7 solution is 1, PS-g-PVBMC-POM beads concentration is 0.5 g/L, aeration rate is 3 L/min, the AO7 solution initial concentration is 0.2 g/L and hydraulic retention time (HRT) is 2 h. With circulation filtration of the solution, 0.5 g/L PS-g-PVBMC-POM beads can degrade 100% of the AO7 solution (0.2 g/L) within 100 min.

Keywords: photocatalytic membrane reactor, dye degradation, polyoxometalate, surface grafting, visible light.

K14 (Invited)

Research on Conductivity of PEO Solid Polymer Electrolyte Doping LCI

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With the merits of high voltage, high specific energy and long cycle life, as well as facilitate the preparation of various shapes of the battery, solid polymer electrolytes are considered as the promising cell component. This research focus on the conductivity of PEO base solid polymer electrolyte doping LCI. LCI and AMPS improve the conductivity of polymer electrolytes by enhancing the compatibility of PEO and PMMA, as well as the molecular complexation of SO_3^{2-} . When the LCI and AMPS contents are increased to 1.0% and 1.3% respectively, the room temperature conductivity reaches the max $4.31\text{E-}8$ S/cm and $1.97\text{E-}6$ S/cm, and then both show downward trend. Furthermore PEO-MMA grafted copolymer has been synthesized with the material of PEO and MMA, research prepare the PEO/MMA grafted copolymer electrolyte film combining blend system research results .Polymerization reaction time and catalyst dosage do have effect on PEO/MMA grafted copolymer electrolyte conductivity, when the polymerization time is 6h, catalyst dosage is 10%, the room temperature conductivity reached the maximum $1.70\text{E-}6$ S/cm.

Keywords: PEO, PMMA, Graft Copolymer, LCI, Conductivity

K15 (Invited)

Crystallization Behaviour, Morphology and Properties of Biodegradable Polymers

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Biodegradable polymers have received more and more attention in the last two decades; however, their relatively poor mechanical properties, slow crystallization rate, and slow degradation rate have limited their further practical application. In our lab, we have been using copolymerization, polymer blending, and the fabrication of polymer nanocomposites to modify the physical properties and extend the application fields of biodegradable polymers. In this topic, I will briefly introduce our recent progress of crystallization behaviour, morphology and properties of biodegradable polymers.

Acknowledgement

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K16

Mutiple Micellization Behaviors of a Dual-Responsive Triarm Star Copolymer for Controlled Release

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A novel light- and temperature-responsive amphiphilic ABC miktoarm star terpolymer consisting of poly(ethylene glycol), poly(2-nitrobenzyl methacrylate), and poly(*N*-isopropylacrylamide) arms, PEG(-*b*-PNBM)-*b*-PNIPAM, was synthesized via a combination of atom transfer radical polymerization (ATRP) and click reaction. In aqueous solution, the ABC miktoarm star terpolymer could self-assemble into spherical micelles consisting of PNBM cores and hybrid PEG/PNIPAM coronas at room temperature, whereas PNBM/PNIPAM cores and PEG coronas at elevated temperatures. The mutiple micellization behaviors of the ABC miktoarm star terpolymer were revealed by transmission electron microscopy (TEM) and dynamic light scattering (DLS). The release of encapsulated fluorescent dye Nile Red from the polymeric micelles could be achieved under stimulation with UV-light irradiation or temperature change. More interestingly, the release could be enhanced under combined stimulation. The prepared dual-responsive polymeric micelles may have great potential in the fields of nanotechnology and biotechnology for controlled release.

K17

Significantly Improving Separation and Antifouling Properties of

Poly(vinylidene fluoride) Membranes through a Hydrogen-Bonded Polydopamine-Polyacryloylmorpholine Layer on the Membrane Surface

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Polyacryloylmorpholine (PACMO), a neutral polymer, which has strong hydrophilicity, has the potential to fabricate antifouling surfaces as hydrogen bond acceptor. In this work, we report the multiple hydrogen bonded interactions of polydopamine (PDA) with PACMO and reveal the mechanism of formation. Taking inspiration from PDA and PACMO interactions, an intrinsic hydrophobic poly(vinylidene fluoride) (PVDF) membrane is modified with a PDA layer and subsequent further immobilized the PACMO via hydrogen bonding as driving force. The hydrophilic PVDF/PDA-PACMO membranes exhibit higher permeability and antifouling performance. The extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) theory derived from surface tension parameters is used to quantitatively elucidate hydrophobicity/hydrophilicity of membranes and membrane fouling mechanisms of bovine serum albumin (BSA) as a model organic foulant. Serendipitously, owing to hydrophilic interaction of surfactant on the membrane surface, it is difficult for oil foulants to attach onto the membrane surface, and consequently the PVDF/PDA-PACMO membranes display significantly enhanced oil-fouling resistance and separation performance. It is also found that the PVDF/PDA-PACMO membranes have satisfying stability and durability due to noncovalent interactions and other potential intermolecular interactions between PDA and PACMO molecules. More general, the versatility of the present strategy facilitates a wide variety of potential applications to develop novel functional coatings based on mussel-inspired intermediate layer, which makes it promising for a straightforward, eco-friendly and more efficient method for material functionalization.

Keywords: polyacryloylmorpholine, polydopamine, membrane functionalization, antifouling, oil/water separation

K18

Excited-state Hydrogen-bonding Dynamics of Camphorsulfonic Acid Doped Polyaniline: A Theoretical Study

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Polyaniline (PANI) with unique conducting and optical property remains one of the most intensely studied conjugated polymers. Despite its long history, the interest shown in PANI has

continued to increase in recent years. The early studies of PANi were mostly focused on the synthesis experiment and the performance analysis as well as the H-band interaction. Nowadays more and more theoretical methods were used to investigate the structure and energetics of various aspects of PANi. Most of recent papers have applied DFT methods to the study of PANi and concluded that these methods are suitable for the modeling, and the theoretical calculation of hydrogen bonding in PANi has been carried out as well. and the investigations were mainly focused on the structural and electronic influences on the hydrogen bonding complexes. However, as far as we know, there are few investigations about the hydrogen-bonding dynamics of hydrogen-bonded PANi acid complexes in electronically excited states. Hence, the study of hydrogen-bonding dynamics in electronically excited states of PANi acid complexes is important.

The Ph₂NH (DPA) and (4-aminocyclohexa-2, 5-dienylidene) phenylamine cation (ICPA) are used to model the distinct amine and iminium nitrogen cation environments in ES respectively, while CSA is modeled by dimethylsulfoxide (DMSO), and the H-bond can be formed between the S=O group of DMSO and the H-N groups of DPA as well as ICPA monomers, which are denoted as DPA-DMSO and ICPA-DMSO hydrogen-bonded complexes respectively. All the electronic structure calculations were carried out using the Gaussian 09 program suite. The ground-state geometric optimization of the isolated DPA, ICPA and DMSO monomers as well as the hydrogen-bonded DPA-DMSO and ICPA-DMSO complexes considered here were carried out using DFT with the B3LYP hybrid functional. The electronic transition energies and corresponding oscillation strengths of all the hydrogen-bonded complexes in their low-lying electronically excited states were calculated using TDDFT with the B3LYP hybrid functional method. The 6-31G+(d, p) was chosen as basis set throughout the whole process.

The equilibrium geometries of the hydrogen-bonded DPA-DMSO and ICPA-DMSO complexes as well as the involved monomers in ground state were calculated. It's obvious that the bond lengths of C6-N1 and C8=N1 groups in the DPA-DMSO or ICPA-DMSO hydrogen-bonded complexes are all shortened compared with their lengths in the DPA and ICPA monomers, and the bond lengths of C13-S1 and C14-S1 groups in the hydrogen-bonded complexes show the shortened tendency compared with their lengths in the DMSO monomer. The electronic excitation energies and the oscillation strengths of the DPA-DMSO, ICPA-DMSO hydrogen-bonded complexes as well as the isolated DPA, ICPA monomers were calculated using TDDFT method. The S₂ state of the hydrogen-bonded DPA-DMSO complex possesses the largest oscillator strength. As a result, the DPA-DMSO complex will be photoexcited to the S₂ state directly. It is obvious that the S₁-S₈ states electronic excitation energies of the DPA-DMSO complex are lower compared with the correspond states of the DPA monomer. In ICPA-DMSO complex, all the electronic

excitation energies of the calculated excited states except for the S1-S3 states are under those of the ICPA monomer, therefore, the hydrogen bond S1=O1...H11-N1 in the ICPA-DMSO complex is strengthened for the S4-S8 states and will bring a redshift. The infrared spectra study is focused on the spectra and vibration of N-H bands in the monomers and the complexes. It's easy to see that the presence of N-H absorption peak at 3635 cm⁻¹ in DPA monomer shifts to 3475cm⁻¹ in DPA-DMSO complex, and the intensity of the vibration is enhanced in the complex. The quite similar conclusion can be drawn that the N-H absorption peak of ICPA-DMSO complex is also enhanced and shifts to 2895cm⁻¹ from 3542cm⁻¹ compared with ICPA monomer. The N-H band is off-plane swing vibration in DPA monomer but is in-plane stretching vibration in DPA-DMSO complex. At the same time, the N-H band is in-plane stretching vibration in both ICPA monomer and ICPA-DMSO complex. From the MOs of DPA-DMSO, it's easy to see that the HOMO orbital possessed the π character, and the LUMO orbital showed the π^* character. As a result, from HOMO to LUMO will be a π - π^* transition. It is obvious that in the MOs of ICPA-DMSO, the electron density is focused on benzenoid ring in HOMO orbital, whereas the quinoid ring in LUMO orbital possesses more electron density, and the electron density transfers from benzenoid ring to quinoid ring during the HOMO to LUMO orbital transition. In addition, it's obvious that the electronic densities of the complex orbitals are mainly distributed on the DPA and ICPA chain.

There were two possible hydrogen bond interactions between DPA/ICPA and DMSO monomers, and the geometric structures were affected by the formation of hydrogen bond, especially the H11-N1 and S1-O1 bonds involved in forming the hydrogen bond, and the stronger hydrogen-bond interaction caused the more obvious band stretch. According to the result of comparing oscillator strength, the DPA-DMSO and ICPA-DMSO complexes were excited to S2 and S3 states respectively. The hydrogen-bond interaction brought the significant redshift of N-H band in the complexes, and the vibration models were also affected by hydrogen-bond formation, especially the N-H band. The S2 state of DPA-DMSO was due to a distinct π - π^* feature, meanwhile there was obvious intramolecular electron density transfer in ICPA-DMSO during the orbital transition from HOMO to LUMO, and the hydrogen bonds were strongly influenced by the charge redistribution which was involved in the orbital transition. Moreover, we noted the phenomenon that only the DPA and ICPA molecules were excited in these states, and the DMSO was stayed in its ground state.