四(4.4',4'',4'''-N,N-二氨基)四苯乙烯光致发光与分子的构象效应

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摘要 利用还原偶联方法合成出新化合物四(4,4',4",4"'-N,N-二氨基)四苯乙烯

( TDETE)。通过测定该化合物在溶液、掺杂聚合物中及晶体粉末的稳态-瞬态荧光光 谱、

荧光量子产率和辐射衰变速率常数等。讨论了分子的构象效应等因素对TDETE

光致发光行为的影响。在一定浓度下TDETE溶液存在着三个发光带,分别为全扭曲 构象分子(位于345nm附近的发光I带)、半扭曲构象分子(位于430nm附近的发光 II带)和激基缔合物(530发光III带)

的辐射衰变所致。在聚合物(PMMA)中,一方面由于分子单键的自由旋转扭曲受到遏制,表现为II带的辐射衰变速率常数(kf值)增大、同时非辐射衰变速率常数knf值减小;另一方面,

TDETE分子之间相互作 用得到加强而有利一缔合物形成,结果,使发光II带和III带合二为一出现强而宽的发射峰,荧光量子产率从溶液中的0.055提高到0.855。此外,在PMM介制裁中观 测到TDETE分子聚集体在

626nm处的发光带(IV),数粉末态中聚集体IV带的强度骤增,峰值波长红移至650nm。

关键词 苯乙烯 P 光致发光 构象 缔合物 聚集体

分类号 0644

# Study on Photoluminescence Behavior and Conformation Effects of Tetrakis-(4,4',4'',4'''-N,N-diethylamino)tetraphenyl Ethylene

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Abstract A new chromophore tetrakis-(4,4',4'',4'''-N,N-diethylamino) tetraphenyl ethylene (abbreviated as TDETE) has been synthesized and characterized by mass spectrum, elemental analysis, 'H NMR spectrum and X-ray diffraction. To understand the influence of molecular conformation upon the photoluminescence properties, absorption/ emission spectra and fluorescence quantum yield  $(\Phi_f)$  as well as the emission dynamics in solution and in PMMA have been investigated. Fluorescence spectrum shows that there are three luminescent bands locating at  $\sim 354$  nm (band II),  $\sim 434$  nm (band III), and  $\sim 534$  nm (band III), respectively, in toluene  $(1*10\sim(-6)\ mol\cdot dm\sim(-3))$  under the excitation of 308 nm. Based on a comparative study of the molecular absorption/emission spectra and of molecular structures by X-ray diffraction and computer simulation, we have confirmed that band I and band II can be assigned to two different conformations resulting from the molecular single bond rotation. Meanwhile band III is attributed to the excimer since its fluorescence intensity is directly proportional to the solution concentration, moreover, its fluorescence intensity becomes much higher in PMMA film and in PMMA rod. Since the free rotation of molecular single bonds is limited and the interaction between molecules is strengthened in the rigid medium, the luminous band II in combination with band III becomes strong and the resultant fluorescence quantum yield is increased from 0.055 in solution to 0.855 in PMMA rod. In addition, the luminescence of molecular aggregation locating at 626 nm in PMMA rod and in PMMA film has been observed (band IV), and it induces the intense photoluminescence with a bathochromic shift to 650 nm in powder state.

Key words STYRENE P PHOTOLUMINESCENCE CONFORMATION ASSOCIATES AGGREGALES

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