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Synthesis of Polyisoprene-*b*-Polystyrene Block Copolymers Bearing a Fluorescent Dye at the Junction by the Combination of Living Anionic Polymerization and Atom Transfer Radical Polymerization

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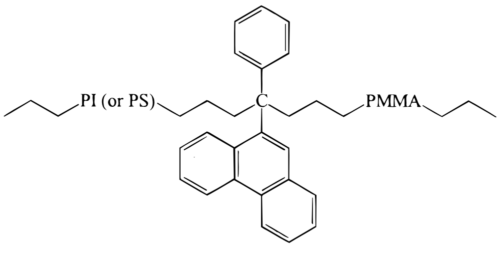
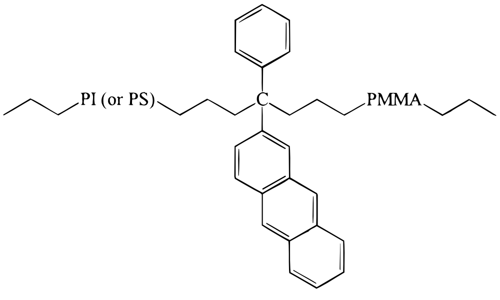
Introduction. In this paper, we describe the synthesis of polyisoprene−polystyrene (PI−PS) block copolymers containing a single fluorescent dye molecule at the junction. It is not possible to prepare junction-labeled PI−PS block copolymers by anionic polymerization alone. We show that one can prepare these block copolymers by anionic polymerization of the PI block followed by atom transfer radical polymerization (ATRP) of the PS block. Block copolymer synthesis through crossover from anionic polymerization to ATRP remains a challenge, and the first report, by Matyjaszewski appeared in 1999.[1] There is a special feature of the reactions we report, because without the dye derivative at the end of the anionic block, little or no block copolymer is obtained.

Diblock copolymers represent a special case of a system composed of two polymer components attached at a common junction. Our interest is in characterizing the width of the interface between the two polymers, either in the bulk state or in selective solvents. We approach this problem through the synthesis of pairs of polymers containing a single fluorescent dye at the block junction: one polymer contains a donor (e.g., phenanthrene, Phe), and the other polymer contains an acceptor dye (e.g., anthracene, An) for direct nonradiative energy transfer (DET) experiments.[2] In DET experiments, the rate and efficiency of energy transfer depends sensitively on the distance between donor and acceptor dyes. As a consequence, a fluorescence decay experiment is sensitive to the distribution of junctions across the interface between the two components.[3] With this technique, we have examined interfaces in poly(styrene-*b*-methyl methacrylate) (PS−PMMA)[4] and poly(isoprene-*b*-methyl methacrylate) (PI−PMMA)[5] in the bulk state and in PI−PMMA micelles in acetonitrile.[6]

Chart 1



Donor



Acceptor

The synthesis of PS−PMMA or PI−PMMA block copolymers (Chart 1) takes advantage of the fact that one can end-cap living polymers of PS and PI with a single molecule of 1,1-diphenylethylene to generate a new and less reactive anion, capable of initiating anionic polymerization of methacrylate monomers. To introduce a fluorescent dye, we used 1-aryl-1-phenylethylene end-caps, in which the aryl group was 9-phenanthyl for the preparation of donor-labeled polymers and 2-anthryl for the preparation of acceptor-labeled polymers. Unfortunately, this approach does not work for the preparation of junction-labeled PI−PS, because the anion formed after addition of the dye derivative is not sufficiently reactive to initiate the polymerization of the second monomer (either styrene or isoprene). We therefore have considered various combinations of two different living polymerization techniques,[7] which could provide access to these novel materials. Over the last several years, a substantial effort has been devoted to the development of controlled ("living") radical polymerization methodologies.[8] Of these, ATRP[8c] seems to be the most robust. ATRP employs various alkyl halides ($R-X$, $X = Cl$, Br) as initiators and a transition-metal complex (e.g., CuX/2,2′-bipyridine) as a catalyst.

To combine anionic polymerization with ATRP (AP-ATRP), one can cap the anionic block with an −OH group and then transform it into α-bromoester,[1,7f] followed by ATRP. For our purposes, we would prefer to avoid an ester group at the junction. To prepare PI-dye-PS block copolymer, the ideal would be to initiate styrene polymerization from the carbon bearing the dye or to have a short spacer such as $-C_6H_4CH_2$- with properties similar to polystyrene. In this paper, we show that PI−PS block copolymers can be prepared if the PI block is capped with the fluorescent dye derivative and then treated with α,α′-dibromo-*p*-xylene, which produces the precursor to ATRP. If one employs 1,1-diphenylethylene (DPE) instead of the dye derivative, the reaction fails because of extensive dimerization of the PI block.

Experimental Section. The dye derivatives, 1-(9-phenanthryl)-1-phenylethylene (**9-Ph**) and 1-(2-anthryl)-1-phenylethylene (**2-An**) were synthesized and purified as described previously[4] and stored in THF in sealed ampules. All polymerizations and chemical reactions were carried out under a nitrogen atmosphere in a flamed-dried glass reactor equipped with a three-way stopcock and a rubber septum. Solvent, initiator, and monomer were transferred into the reactors through a stainless steel cannula or a syringe. Isoprene (at 2−5 vol %) was polymerized with *sec*-butyllithium in cyclohexane at 40 °C for 2 h. After the polymerization was completed, the polymerization solution was cooled to 0 °C and then reacted with 1.2 equiv of **9-Ph** or **2-An** in THF/cyclohexane (1/1, v/v). The reaction was kept at 0

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Chart 2

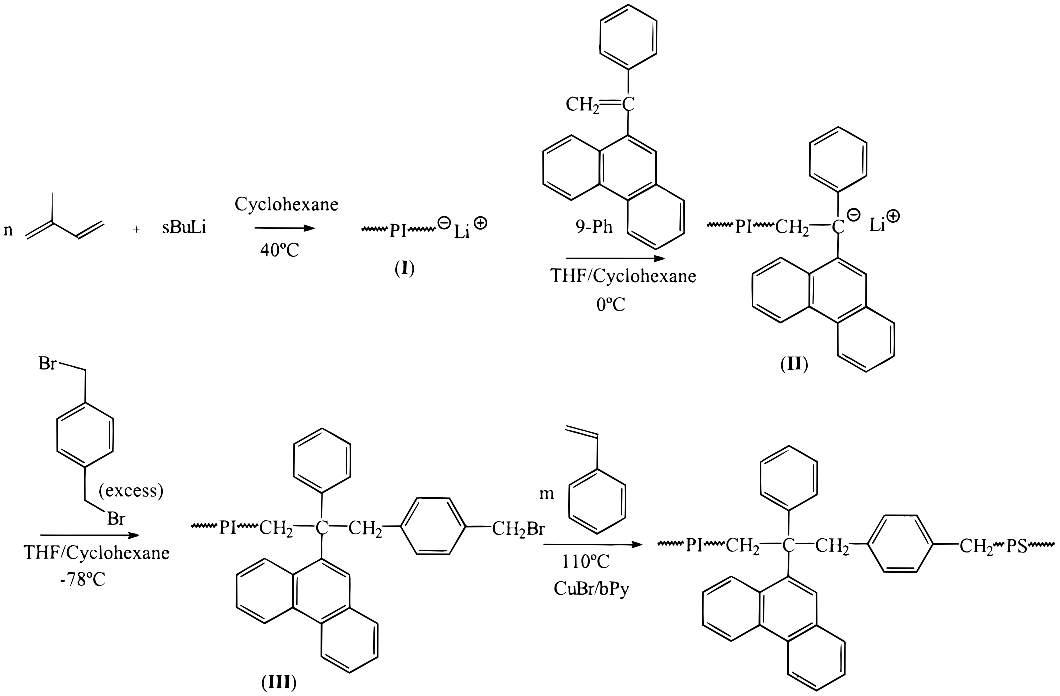


Table 1. Characteristics of PI End-Capped with a Fluorescence Dye[a]

	PI			PI dye		
sample	$M_{n\ theo}$[b]	M_n(GPC)[c]	M_w/M_n[c]	M_n(GPC)[c]	M_w/M_n[c]	dye/polymer[d]
1, PI−(9-Ph)	2500	2800	1.04	3300	1.04	>0.95
1′, (PI-9-Ph)	2500	2430	1.05	2500	1.05	>0.95
2, PI−(9-Ph)	8000	8400	1.03	8900	1.03	
3, PI−(2-An)	7000	7200	1.03	7400	1.03	

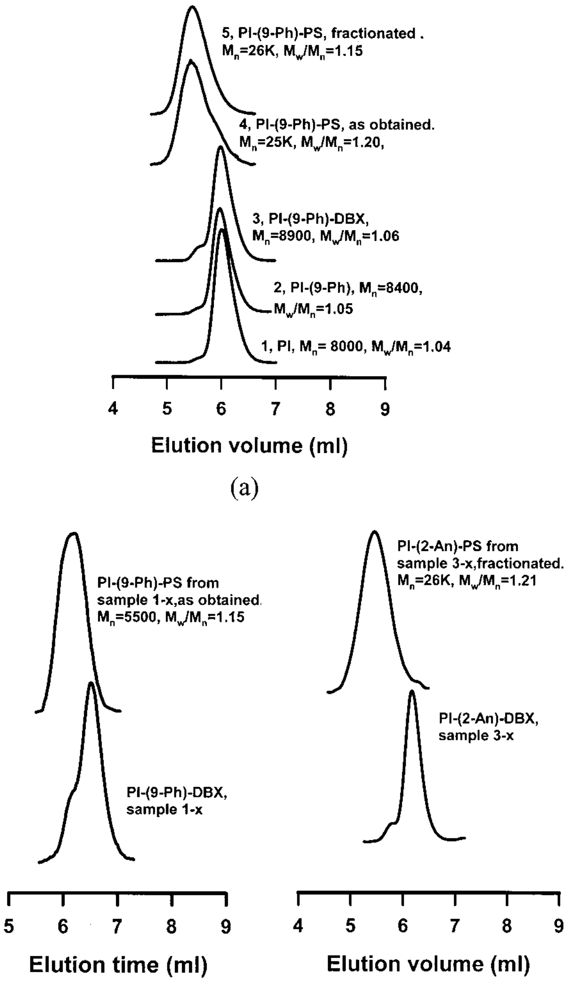
[a] Data obtained from an aliquot of polymer from the living system: [dye]/[*sec*-BuLi] = 1.2 [b] Calculated based on the mole ratio of isoprene to *sec*-BuLi. [c] Obtained by using PI standards. [d] On the basis of integration of the ^{1}H NMR signal

°C for 20 min and then cooled to −78 °C. The mixture was then slowly added to a THF solution containing an excess of α,α′-dibromo-*p*-xylene (DBX) or α,α′-dichloro-*p*-xylene (DCX) at −78 °C. After 5 min at − 78 °C, this solution was quenched with degassed methanol, and then the polymer was precipitated in methanol. The polymer was purified by repeated precipitation and then vacuum-dried. ATRP of styrene was initiated with the benzyl bromide-end-capped polyisoprene and catalyzed by CuBr/bpy. The polymerization was carried out in liquid styrene at 110 °C under a nitrogen atmosphere in a sealed tube.[8c]

^{1}H NMR spectra were recorded on a Varian spectrometer at 500 MHz in $CDCl_3$ at 23 °C and in $C_6D_4Cl_2$ at 120 °C. Molecular weights were obtained from gel permeation chromatography (GPC) experiments at 35 °C, using THF as the eluent, monitored with tandem fluorescence and differential refractometer detectors. Calibration curves were prepared with both PS and PI standards (Polymer Source Inc.). UV absorption measurements were carried out in $CHCl_3$. M_n(UV) values for Phe-containing polymers were calculated using ϵ_{300} = 9400 L/mol cm reported for 1-(9-phenanthryl-1-phenyl ethane) EPheH.[4]

Results and Discussion. This paper describes the synthesis of PI−PS diblock copolymers labeled at the junction with a single fluorescent dye. In the synthesis, the PI carbanion is first reacted with a 1-aryl-1-phenyl ethylene derivative and then treated with an excess of DBX. This approach, shown in Chart 2, provides a polymer with a benzylic bromide end group suitable for initiating the polymerization of styrene by ATRP. Anionic polymerization of isoprene in cyclohexane proceeds in a typical living fashion. Upon the addition of the **9-Ph** or **2-An** in THF, the color of the reaction mixture changes immediately from faint yellow to deep blue (**9-Ph**) or purple (**2-An**). These monomers, like DPE or other structurally similar molecules (e.g., 1-(1-naphthyl)-1-phenylethylene[9] and 1-(1-pyrenyl)-1-phenylethylene[10]), do not polymerize under the present reaction conditions. Only one dye molecule adds to each polymer, meeting one key requirement for an effective DET experiment.[4] To analyze each step of the reaction, aliquots of the reaction mixture before and after addition of the dye derivative were removed and quenched with methanol. Their characteristics are reported in Table 1. The polymers before and after addition of the dye derivative have essentially identical GPC traces in the RI detector (Figure 1a, traces 1 and 2), but the dye-labeled polymer can also be monitored with the tandem fluorescence (FL) detector.

ATRP of styrene generally requires an alkyl halide and, preferably, a benzylic halide[8c] as an initiator. The reaction of living anionic polymers with α,ω-dihaloalkanes to prepare halogen-end-capped polymers has been investigated previously. Most authors report a large extent of polymer dimerization, resulting from the metal−halogen interchange process,[11] in competition with the end-capping reaction. For example, Burgess and Richards[12] report that 75% dimer is formed in the



(a)

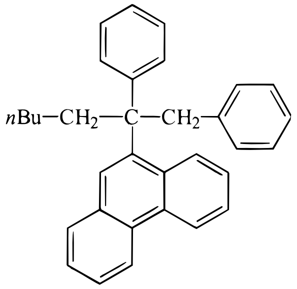
(b) (c)

Figure 1. GPC traces for the junction-labeled PI−PS block copolymers and their precursors. (a) GPC traces (RI signal) of each step in the synthesis of the 2-xa series samples. Bottom-to-top: PI aliquot from the first step, after end-capping with **9-Phe**, after reaction with DBX, after ATRP of styrene, and after purification with hexane. (b) GPC traces (fluorescence signal) of ATRP of sample 1-x and its precursor. (c) GPC traces (RI signal) of ATRP of sample 3-x and its precursor.

reaction of DBX with polystyrenyllithium. Young et al.[13] examined the reaction of polybutadienyllithium with an excess of 1,2-dibromoethane and found 76% of dimeric product. Recently, Hirao et al.[14] investigated the reaction of 1,3-dihalopropanes with polyisoprenyllithium and polystyrenyllithium. With dichloropropane, they found covalent bond formation as the major product, and the $-CH_2Cl$ end group could be detected in the ^{1}H NMR. For dibromopropane, dimer formation dominated, but they found that by end-capping the living polymers with DPE, dimer formation in the reaction with 1,3-dibromopropane could be substantially suppressed.

DPE, like **9-Ph** and **2-An**, is an effective end-capping agent for anionically polymerized PI and PS. In Table 2, we show the results of the termination reaction of living PI and PS, after first reacting them with DPE and then with an excess of DCX or DBX. In all of the cases, the dark red color of the 1,1-diphenylalkyl carbanion disappeared immediately on mixing at −78 °C with the xylene dihalide. In the case of DCX, with Cl as the halogen group (sample 4, Table 2), virtually no dimer formation was observed in the GPC trace. End group analysis by ^{1}H NMR shows quantitative end-capping by DCX. When the DPE-modified PI anion was reacted with excess DBX, a large fraction of dimer was found, regardless of whether we added DBX to the living PI−DPE solution or added the living polymer to the DBX solution. When we compare our result for the reaction of PS−DPE anion with DBX (sample 8, Table 2) to that reported by Burgess and Richards[12] for the direct reaction of polystyrenyllithium with DBX, we find a significant reduction in dimeric product (8% vs 75%). Unfortunately, DPE is not as effective at suppressing dimer formation for reactions of polyisoprenyllithium with DBX.

In contrast, capping the living PI with **9-Ph** or **2-An** prior to reaction with DBX leads to a substantial reduction in dimer formation. For example, the reaction of the **2-An**-modified PI anion with excess of DBX proceeded efficiently, and only a trace (5%) of dimer could be detected (sample 3-x, Table 2). In the case of the **9-Ph**-end-capped PI anion, the coupling reaction (5% for sample 2-xa and 4% for sample 2-xb, Table 2) was also largely reduced compared to that of PI-DPE, although a relatively higher dimer yield (15%) was observed for sample 1-x.[15] The end groups of samples 2-xa and 3-x were analyzed by ^{1}H NMR. At room temperature, the $-C\mathbf{H}_2-$Ph signal is too broad to be detected although the $-C\mathbf{H}_2$Br is visible. By running the spectrum at 120 °C in dichlorobenzene-d_4, we can observe the two signals at 3.6 and 3.8 ppm (Figure 2) of the $-C\mathbf{H}_2-$Ph group. The assignment of these signals is based on the ^{1}H NMR spectrum of the model compound BPheB, which is prepared by the reaction of 1-(9-phenanthryl)-1-phenyl-hexyllithium with excess of benzyl bromide.[16] The signal at 6.4 ppm, which comes from two of the aromatic protons of the attached DBX (Figure 2), is also a signature of termination by DBX. Careful integration of the signals at 6.4 and 8.5 ppm (two protons from phenanthryl group) shows a 1:1 intensity ratio, supporting the inference of quantitative end-capping. Finally, UV absorption measurements (300 nm) of sample 2-xa gives M_n(UV) = 8930, in accord with M_n(GPC) = 10 000 (PI standards). The major conclusion we draw from these experiments is that the presence of the polycyclic aromatic ring adjacent to the carbanion center suppresses the dimerization reaction or enhances the substitution reaction with DBX, to yield polymers with an end group suitable for initiating ATRP.



BPheB

ATRP of Styrene Initiated by PI Macroinitiator. The PI samples 1-x, 2-xa, and 3-x (Table 2) were used as macroinitiators for the controlled ATRP of styrene, using a catalyst based on CuBr and 2,2′-bipyridine. GPC traces of the starting PI macroinitiator and the resulting block copolymer for sample 1-x are presented in Figure 1b. The shift of fluorescent signal to smaller elution volume (higher molecular weight), without any notice-

Table 2. Reactions of Living Polymers End-capped with DPE with α,α′-Dihalo-*p*-xylene[a]

living polymers[b]	halogen X	[T]/[Li][c]	temp (°C)	termin.[d]	GPC result[e]		
					M_w/M_n	P%	P−P%
4, PI-DPE	Cl	4	−78	N	1.08	97	3
5, PI-DPE	Br	6	−78	R	1.06	5	95
6, PI-DPE	Br	5	0	N	1.15	35	65
7, PI-DPE	Br	6	−78	N	1.15	40	60
8, PS-DPE	Br	6	−78	R	1.06	92	8
1-x, PI−(9-Ph)[f]	Br	3	−78	N	1.12	85	15
1′-x, PI(9-Ph)[f]	Cl	9	−78	N	1.08	100	0
2-xa, PI−(9-Ph)[g]	Br	3	−78	N	1.06	95	5
2-xb, PI−(9-Ph)[g]	Br	6	−78	N	1.05	96	4
3-x, PI−(2-An)[h]	Br	6	−78	N	1.06	95	5

[a] Reactions were carried out in THF or THF/cyclohexane mixture (1/1, v/v). [b] M_n values of PI-DPE were in the range of 2500−3500, M_n of PS is 10 000. M_w/M_n values were less than 1.10. [c] Molar ratio of α,α′-dihalo-*p*-xylene/anion; [T] refers to the concentration of DBX or DCX. [d] N indicates a normal addition order; R indicates a reverse addition order. [e] P indicates the yield of monoadduct and P−P indicates the yield of dimeric product. [f] From sample 1. [g] From sample 2. [h] From sample 3.

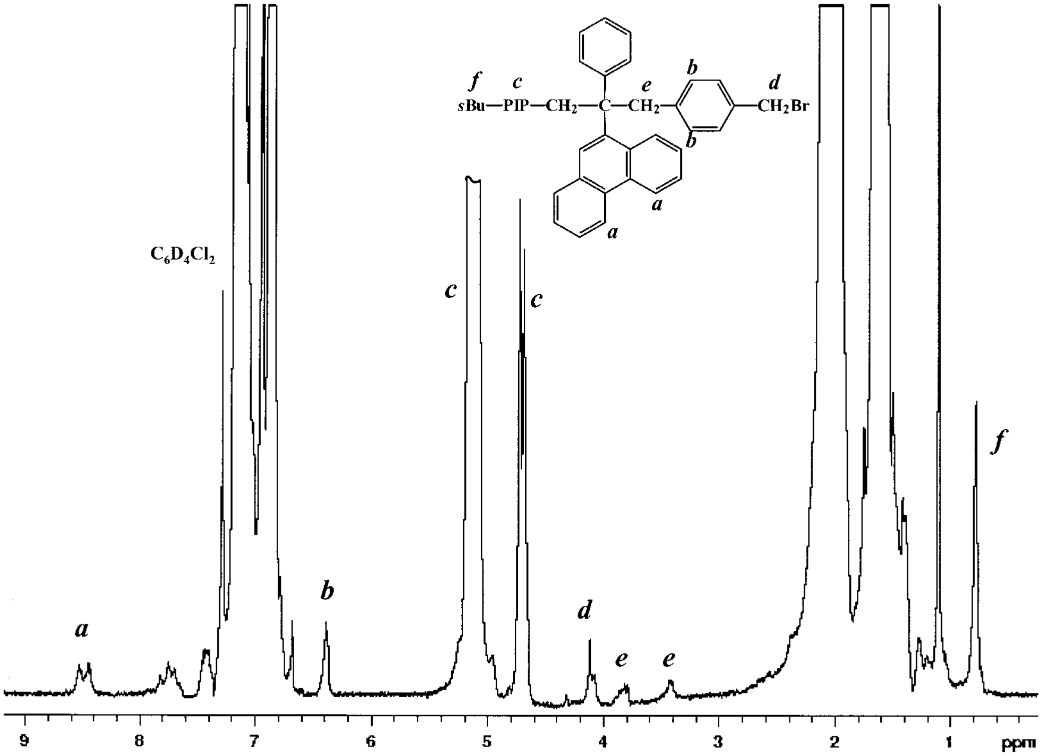


Figure 2. 500 MHz ^{1}H NMR spectrum for sample 2-xa at 120 °C in dichlorobenzene-d_4.

able shoulder or tail in the trace, indicates the formation of a block copolymer. Because sample 1-x was contaminated with ca. 15% dimer, which cannot initiate the ATRP of styrene, the peak due to the dimer (a shoulder in the GPC trace of sample 1-x) must be hidden under the block copolymer signal. We do find that some of the PI is inefficient in initiating ATRP of styrene, as indicated by the slight tail in Figure 1a (trace 4). This situation has been improved by using a homogeneous catalyst (CuBr/dHbPy).[17] Nevertheless, the unreacted PI (including the dimer) can be completely removed from the block copolymers with an alkane solvent such as hexane. GPC traces of the purified PI-*b*-PS block copolymers, prepared from sample 2-xa and 3-x, are shown in parts a (trace 5) and c of Figure 1. The structure of block copolymer obtained from sample 2-xa is confirmed by ^{1}H NMR. A combination of NMR and GPC measurements gives $M_n = 45\ 000$, which compares favorably with $M_n(\mathrm{UV}) = 38\ 000$. We conclude that well-defined PI-*b*-PS block copolymers with a single fluorescence dye at the junction can be prepared by the combination of AP and ATRP techniques.

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Supporting Information Available: ^{1}H NMR spectra of the end-capped polyisoprene block and of the model compounds BPheH and BPheB, and GPC traces of PI−dye−PS obtained using CuBr/dHpby as a homogeneous catalyst for styrene polymerization. This material is available free of charge via the Internet at htpp://pubs.acs.org.

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(15) The solubility of DBX in THF at −78° is poor. In the case of 2500 M_n PI, part of the DBX was precipitated in THF at −78 °C, resulting in less DBX in THF solution. This did not happen when high-MW PI was used. Therefore, we speculate that the coupling reaction here is a result of substitution at both $-CH_2Br$ groups of DBX.

(16) The doublet of doublets (3.6, 3.8 ppm) seen for the $-CH_2-$Ph group is a consequence of the adjacent chiral center. In the DPE-end-capped polymer, which lacks a chiral center, one finds a broad singlet in this region of the spectrum.

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