润后，置于密封容器过夜。然后分别用二次水和无水乙醇清洗，吹干。处理后，可明显提高电池的短路电流[9]。将该电极再次置于马弗炉内 450° C 煅烧 30 分钟。

TiO_2表面吸附的染料是通过将成膜后的电极浸泡到 3 $\times 10^{-4}$ M 的 Cy9 的无水乙醇和无水乙腈的混合物（体积比为 1：1）溶液或 N719 的 DMF 溶液中 12h。当电极还没有完全冷却的情况下立即浸入染料溶液里，以避免TiO_2表面再次吸水或由于毛细作用将周围空气中的水蒸气冷凝后进入多孔膜的孔内。孔内水的存在会降低染料电子的注入效率。通常在电极大约降到 80 ° C 左右时浸入染料溶液中。完成染料的吸附后，将电极从溶液中取出，用无水乙醇彻底清洗，以电吹风吹干。然后，以镀铂导电玻璃为对电极，用 KC-904 热熔胶（科琪，上海）和 HY-914 粘合剂组装 DSSCs。

太阳能电池的有效面积为 0.15 cm^2。光强使用光功率计测定。本工作所使用的电解质及其组分如表 6.1 所示。电解质的所有成分的浓度的计算都是以离子液体（RMIL）的体积计算的。它们的固化过程是在玛瑙研钵中实现的。

表 6.1 各种电解质及其组成

Table 6.1 the electrolytes and their ingredients

电解质	I_2/M	LiI/M	guanidinium thiocyanate/M	*t*-BP/M	RMIL	SiO_2
E1	0.5		0.1		BMII	5wt%
E2	0.5		0.1	1	BMII	5wt%
E3	0.5	0.1	0.1		BMII	5wt%
E4	0.5	0.1	0.1	1	BMII	5wt%

6.3 结果与讨论

6.3.1 吸收和氧化还原特性

图6.1为染料Cy9在乙腈和无水乙醇的混合溶液（体积比 1：1）和N719在DMF溶液中（1×10^{-5}M）的紫外-可见吸收光谱以及分别以590nm和529nm的光激发的荧光发射光谱。由图6.1可知，在溶液中，N719的吸收峰分别在521nm和374nm，Cy9的分别在555nm和590nm。N719和Cy9的发射峰分别位于632nm和630nm。各个吸收峰对应的摩尔消光系数列于表6.2。对于N719染料，其吸收光谱几乎覆盖了整个可见光区，这也是该染料具有高的光电转换效率的原因之一。两个染料在吸收峰处对应的最大摩尔消光系数由其吸收光谱得到并列于表6.2。由表6.2可知，Cy9的摩尔消光系数比N719高近一个数量级。高的摩尔消光系数也是好多纯有机染料相对Ru(II)复合物的优势所在，因为高的摩尔消光系数有利于DSSCs的光捕获效率的提高，也使得以较薄的膜而获得较高的光电转换效率成为可能。表6.2也给出了每一个染料的最高占有轨道（HOMO）和最低未占有轨道（LUMO），两能级是由它们的循环伏安曲线以及吸收光谱的边带吸收估算出来的。从能级上看，N719的LUMO能级较Cy9的更负。下边我们根据两个染料以及TiO_2的光物理特性计算了两种染料受光激发后向TiO_2导带转移电子的自由能变化。

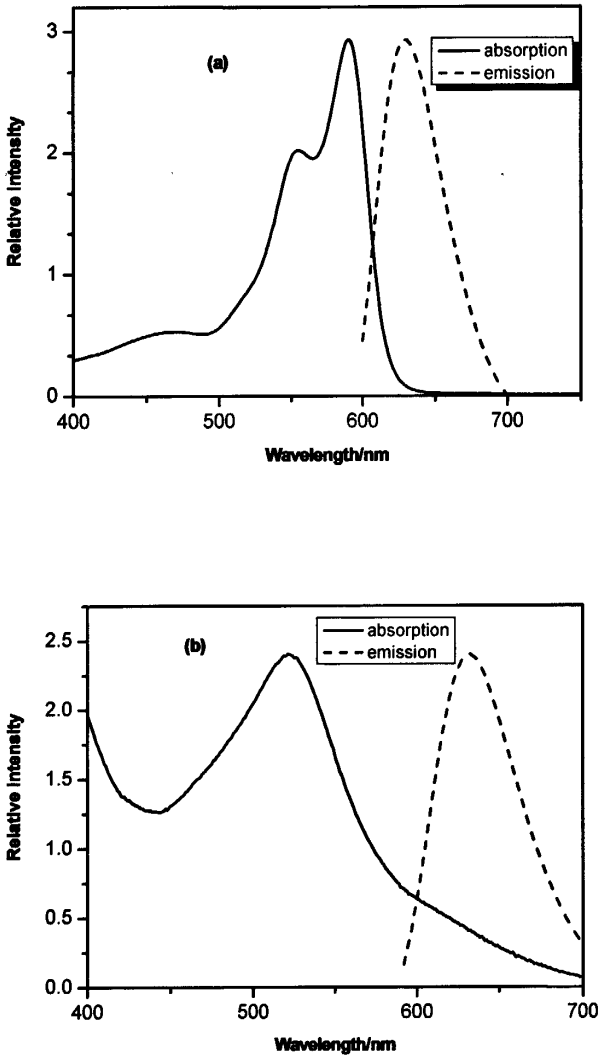


图 6.1 Cy9（a）的乙醇和乙腈混合溶液（1×10^{-5}M）和 N719（b）的DMF溶液（1×10^{-5}M）的吸收和发射光谱，光路长度为1cm，激发波长分别为590nm和529nm

Fig. 6.1 Absorption and emission spectra of Cy9(a) in 1×10^{-5}M acetonitrile and ethanol mixture solution (volume ratio: 1:1) and of N719 in 1×10^{-5}M DMF solution. Optical pathlength was 1 cm. Excitation wavelength for the luminescence were 590nm and 529nm, respectively.

两种染料受光激发后向TiO_2导带转移电子的自由能变化可由Rehm-weller[48]方程计算：

$$\Delta G = E_{ox}(\mathrm{D}) - E_R(\mathrm{A}) - E_{0\text{-}0} - C \qquad (6.1)$$

其中E_{ox}(D)为给体分子的氧化电位，即敏化剂染料的氧化电位；E_R(A)为受体分子的还原电位即TiO_2纳米晶薄膜的平带电位；$E_{0\text{-}0}$为给体分子振动基态和振动激发态间的激发能，

可由吸收光谱和荧光发射光谱确定；C为溶剂对给体分子氧化态（D^+）和受体分子还原态的库仑稳定能，对于极性溶剂一般取0.06eV。

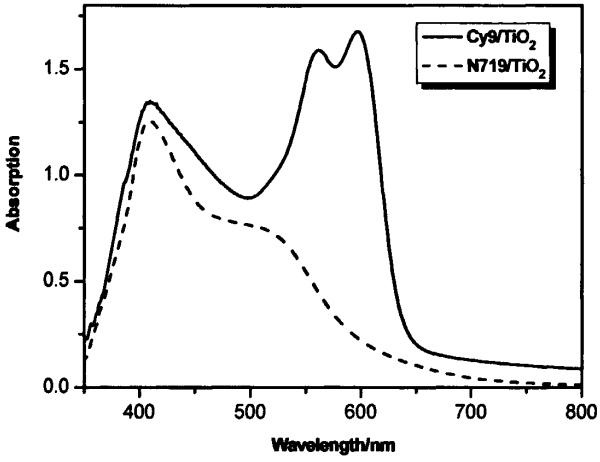


图 6.2 Cy9(实线)和N719(虚线)吸附在TiO_2膜上的的紫外-可见吸收光谱.

Fig. 2 UV-vis Absorption spectrum of Cy9 (solid line) and N917 (dash line) absorbed on nanocrystalline TiO_2 thin films

Cy9和N719的氧化电位分别为-0.68V和-0.65V（vs.NHE）；根据文献[48]，TiO_2纳米晶薄膜的平带电位为-0.55V（vs. SCE），由于SCE电极的标准电位为0.2412V（vs.NHE），所以，TiO_2纳米晶薄膜的平带电位相对标准氢电极为-0.31V；$E_{0\text{-}0}$由图6.1确定，对于Cy9和N719分别为2.04和2.07eV。将上述数值分别代入方程6.1可得到Cy9和N719受光激发后向TiO_2导带转移电子的自由能变化分别计为ΔG_C和ΔG_N，分别为-0.56eV和-0.87eV。这说明两种染料在光激发情况下向TiO_2导带注入电子的过程是热力学可行的。

表 6.2 Cy9在乙腈和无水乙醇混合溶液中（体积比 1：1）和N719 DMF溶液中（1×10^{-5}M）的光特性数据及其能级

Table 6.2 Optical properties for Cy9 in 1×10^{-5}M acetonitrile and ethanol mixture solution (volume ratio: 1:1) and for N719 in 1×10^{-5}M DMF solution and energy levels for them.

dye	λ_{max1}	ε_1	λ_{max2}	ε_2	HOMO(eV)	LUMO(eV)
N719	375	1.13×10^4	521	1.07×10^4	-5.45	-3.85
Cy9	555	1.01×10^5	590	1.50×10^5	-5.73	-3.82

6.3.2 染料敏化太阳能电池的光电化学行为

图 6.3 为分别由 N719 和 Cy9 敏化的 TiO_2 膜的光电流作用谱。激发光是透过导电玻璃基底照射到负载染料的 TiO_2 膜上的。图 6.2 为 Cy9 和 N719 吸附在纳米 TiO_2 膜上的紫外－可见吸收光谱。由图 6.2 和 6.3 可以看出，染料敏化太阳能电池的光电流作用谱与

敏化剂的紫外-可见光谱及其相似，这也从另一角度证明器件的光电流由所负载的敏化剂受光激发而产生的。与溶液中的紫外-可见吸收光谱不同的是，由 Cy9 敏化的 TiO_2 膜的紫外-可见吸收光谱以及光电流作用谱同时向蓝光及红光两个方向拓展，这意味着染料在 TiO_2 表面形成一定的聚集态。我们知道，菁染料在溶液中或固液表面由于强的分子间力而具有强烈的聚集趋势。染料的聚集通常有三种形式：使吸收光谱红移的 J-聚集，蓝移的 H-聚集和即发生红移又发生蓝移的人字形（Herring-bone）聚集[189]。实验结果表明，本工作中所使用的 Cy9 染料在 TiO_2 纳米晶表面形成人字形聚集。

另外，由图 6.3 还可以看出，N719 敏化的 DSSCs 的 IPCE 值在 490nm-540nm 光谱范围内超过 80%，460nm-560nm 范围内超过 60%，在 520nm 处达到最大值 82.3%。这在准固态 DSSCs 中是较高的。对于 Cy9，可喜的是在 520-630nm 范围内出现了一个大于 30%的平台，但总体上看是较低的。对于这两种在紫外吸收和能级轨道等方面都具有一定的可比性的敏化剂，光电特性却相差较大，这就要从另外的角度对其进行剖析了。从电流产生的过程考虑 IPCE 也可表示为光捕获效率(LHE(λ))，电子注入量子效率（$\phi_{inj}(\lambda)$）及注入电子在纳米晶膜与导电玻璃的后接触面(back contact)上的收集效率（$\eta_c(\lambda)$）三部分相关。见公式(6.2)：

$$IPCE = LHE(\lambda)\ \phi_{inj}(\lambda)\ \eta_c(\lambda) = LHE(\lambda) \times \phi(\lambda) \qquad (6.2)$$

其中$\phi_{inj} \times \eta_c$可以看作量子效率$\phi(\lambda)$。

首先，我们分别对两种染料的光捕获效率进行了测试。分别配制两种染料的五个不同浓度的溶液，分别测定它们的紫外-可见吸收光谱，得到 Cy9 和 N719 的平均最大摩尔消光系数（ε）（以第二吸收峰计算）分别为 $8.37\times10^4\ M^{-1}cm^{-1}$、$1.06\times10^4\ M^{-1}cm^{-1}$。有了平均摩尔消光系数就可以利用电极浸泡前后吸光度的变化来计算染料溶液的浓度变化，进而计算它们的吸附量。分别提取电极浸泡前后的染料溶液 1mL 并稀释至 10mL，测其紫外-可见吸收光谱，根据前后吸光度的差值利用平均摩尔消光系数反推出浓度差，根据溶液体积和电极面积进而计算出单位面积的吸附量（Γ）。结果表明，Cy9 和 N719 的吸附量分别为 1.43×10^{-8} mol cm^{-2}和 8.70×10^{-8} mol cm^{-2}。利用摩尔消光系数（ε）和单位面积吸附量（Γ）根据公式（6.3）可以求得最大吸收波长处的光捕获效率(LHE)[232]：

$$LHE(\lambda) = 1 - 10^{-[1000(cm^3L^{-1})\cdot\varepsilon(mol^{-1}\cdot L\cdot cm^{-1})\cdot\Gamma(mol\cdot cm^{-2})]} \qquad (6.3)$$

把以上测试结果代入上式得Cy9与N719最大吸收波长处的光捕获效率分别为0.936和0.880。

这表明染料Cy9在光电转换方面确实有其优势所在，它的光捕获效率比标准染料N719还要高。那么根据公式6.2，Cy9和N719最大吸收波长处的量子效率$\phi_C(\lambda)$和$\phi_N(\lambda_{max})$分别为：

$$\phi_C(\lambda_{max}) = IPCE_C(\lambda_{max}) / LHE_C(\lambda_{max}) = 39.5\%$$

$\phi_N(\lambda_{max})=IPCE_N(\lambda_{max})/LHE_N(\lambda_{max})=93.5\%$

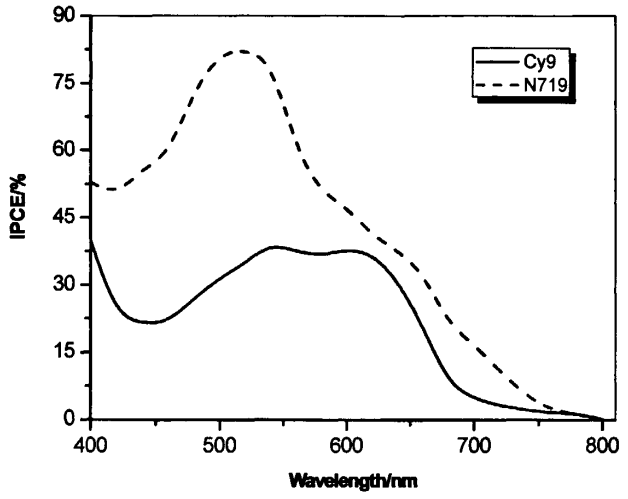


图6.3 由N719（虚线）和Cy9（实线）敏化的TiO_2电极的光电流作用谱，以E1为电解质

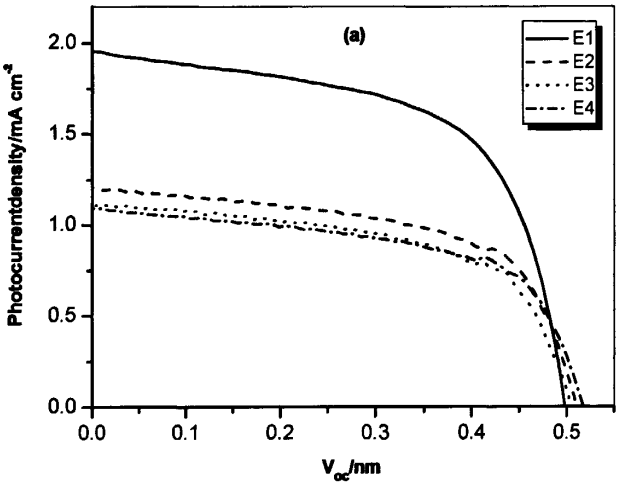
Fig. 6.3 Photocurrent action spectra of the TiO_2 electrodes sensitized with N719 (dot line) and Cy9 (solid line), E1 as electrolyte.

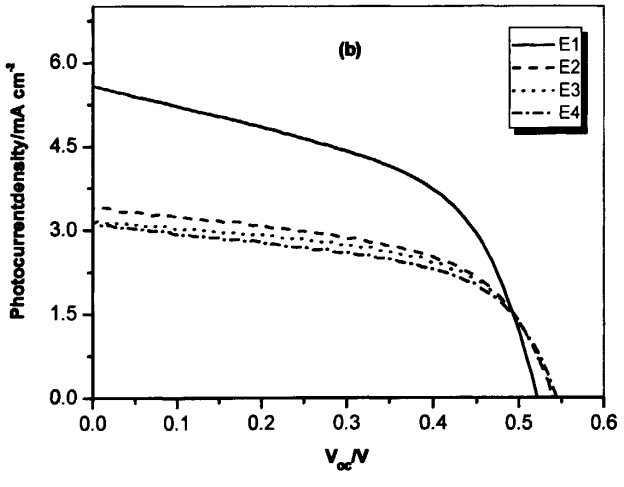
看来Cy9敏化的DSSCs的量子效率要比N719敏化的小得多。而对于所有染料，激发态寿命的数量级为纳秒级，比电子的注入速度高约三个数量级，因此，ϕ_{inj}对于研究的所有染料敏化电极相差无几而且很高[233]。所以导致Cy9低的光电转换效率的原因只有低的η_c。而电子的反向复合是影响电子收集效率的重要因素。由于所有测试条件一致，所以低的电子收集效率是在准固态DSSCs中由于Cy9的立体结构及其能级而导致的电子回传而引起的。

接着，我们在表征两种染料敏化的太阳能电池的光电流-电压特性的同时，改变不同的准固态电解质，研究了电解质成分及其光强对光电特性的影响，如图6.4和6.5所示。对单一电解质而言，结果是和IPCE的结果相一致的，即Cy9敏化的DSSCs的光电流密度J_{sc}，光电压V_{oc}和转换效率η比N719要小。使用对于Cy9而言效率最高的电解质E1，在100mW cm^{-2}的光强下，转换效率只达到1.70%，电流密度、开路电压和填充因子分别为6.81mA cm^{-2}、520mV和0.48。而N719的效率却达到4.45%，电流密度、开路电压和填充因子分别为11.76mA cm^{-2}、640mV和0.59。而当光强发生改变时，在20mW cm^{-2}、75 mW cm^{-2}和100 mW cm^{-2}下，使用E1电解质，Cy9敏化的DSSCs的效率分别为2.96%、2.01%和1.70%，而N719敏化的DSSCs的效率分别为5.88%、5.21%和4.45%。另外我们也可以看出，所有DSSCs的转换效率随光强的增加而降低，使用其他电解质也有同样的规律性。这是因为DSSCs并不像硅基太阳能电池具有稳定的光电化学行为，它们对光强的变化非常敏感。当光强增强时，I_3^-/I^-在工作电极与对电极间的迁移速率不足以满足对染料氧化

态的还原[30]。这样，离子的扩散过程就成为光电流产生的控制步骤。所有光电特性数据均列于表6.3。

为了使电池的效率进一步提高，我们在电解质E1的基础上引入其他成分，其中E2中加入了4-叔丁基吡啶（t-BP），在E3中引入LiI，而在E4中同时引入这两种成分。图6.4为采用这四种电解质的Cy9敏化的太阳能电池的光电流-电压特性曲线。由图6.4可知，两种成分的引入，虽然使开路电压略微增大，但光电流却有所降低。*t*-BP加入的结果与液体电池的测试结果是一致的。菁染料使用含有*t*-BP电解液进行光电特性测试时，光电流会大幅下降。而对于LiI，目前在DSSCs的研究中抗衡阳原子用的最多的就是Li^+和咪唑类阳离子[124,125,120b]。所以，根据公式1.15，LiI的加入导致电流的降低很可能是因为I^-浓度的增大改变了电解质的氧化还原电位，从而影响了染料氧化态的还原速度。





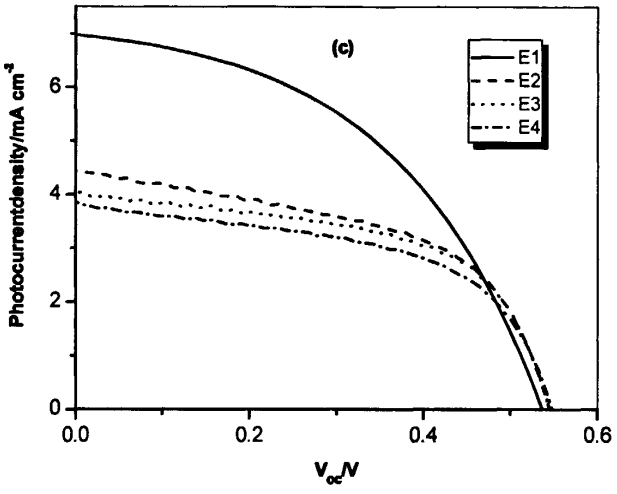
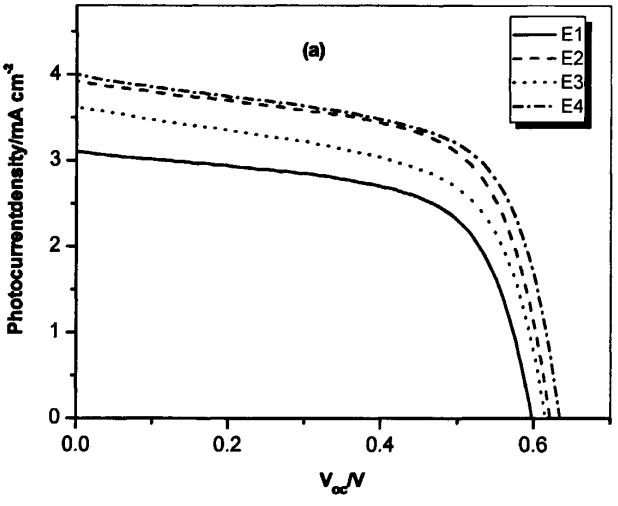


图 6.4 由Cy9敏化的太阳能电池在不同光强下的光电流-电压特性曲线（a）20 mW cm^{-2}（b）75 mW cm^{-2}（c）100 mW cm^{-2}，白光光源为500W氙灯

Fig. 6.4 Photocurrent-voltage characteristics for solar cells sensitized by Cy9 under different irradiation intensity of 20 mW cm^{-2} (a), 75 mW cm^{-2} (b) and100 mW cm^{-2}, white light from a 500W xenon lamp

图6.5给出了电解质成分的改变对N719敏化的DSSCs的光电特性的影响。与Cy9相反，各种成分的引入使电池的开路电压增大的同时，短路电流却有所提高。无疑，转换效率也随之提高。*t*-BP的加入，在液体电解质的研究中认为由于*t*-BP可以通过吡啶环上的N与TiO_2膜表面上不完全配位的Ti配合，阻碍了导带电子在TiO_2膜表面与溶液中I_3^-复合，可明显提高太阳电池的开路电压、填充因子和光电转换效率[126, 127]。如表6.3所示，这里填充因子的改变是不明显的，所以我们认为t-BP的加入除起到上述作用外，还由于



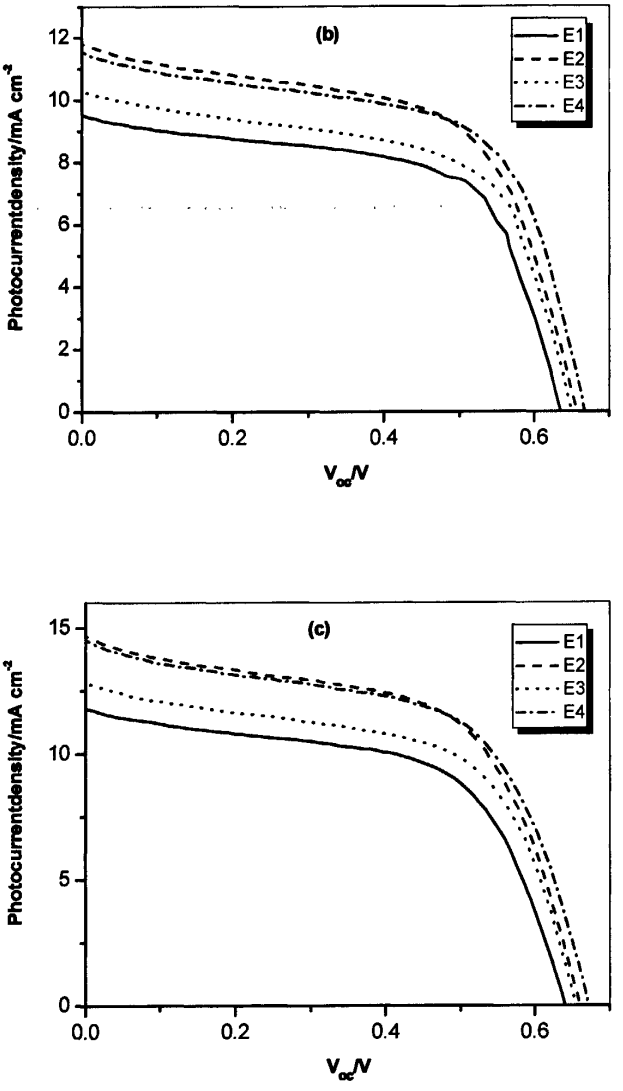


图 6.5 由N719敏化的太阳能电池在不同光强下的光电流-电压特性曲线（a）20 mW cm^{-2}（b）75 mW cm^{-2}（c）100 mW cm^{-2}，白光光源为500W氙灯

Fig. 6.5 Photocurrent-voltage characteristics for solar cells sensitized by N719 under different irradiation intensity of 20 mW cm^{-2} (a), 75 mW cm^{-2} (b) and 100 mW cm^{-2} (c), white light from a 500W xenon lamp

降低了电解质的粘度，增加了电解质的导电性而提高了光生电流的。而LiI的加入，增加了I$^-$的浓度，同时引入小体积的抗衡阳离子，在改变了电解质的能级的同时，也改变了染料氧化态的还原速率。由于N719的HOMO轨道与Cy9不同，所以这种改变反而使光电流和电压有所增加。

为了表明我们所研究的准固态电解质的优越性，另外由于N719为标准染料，我们选

Cy9为敏化剂进行了稳定性测试。在1000h内，以光强为75 mW cm^{-2}的白光对其各个参数进行了表征，如图6.6所示。该器件表现出很好的稳定性，1000小时内转换效率起初不断增加，300h后基本保持稳定。效率的增加主要是电流的贡献，开路电压随时间变化不大。我们认为，这是因为准固态电解质在TiO_2多孔膜的扩散比较慢，与各个组件达到很好的电接触需要一定的时间。另外从敏化剂的角度来考虑，虽然该染料敏化的准固态DSSCs总的光电转换效率较低，但是表现出如此好的稳定性。这对于我们以后设计稳定的纯有机敏化剂具有很好的参考价值。

表 6.3 由N719和Cy9敏化的太阳能电池采用不同的准固态电解质在不同的光强下的光电特性数据

Table 6.3 Parameters of solar cells sensitized with N719 and Cy9 under different irradiation intensity for different quasi-solid electrolyte.

	Sensitizers	Electrolyte	J_{sc}(mA cm^{-2})	V_{oc}(mV)	*FF*	η
20 mW cm^{-2}	N719	E1	3.06	600	0.64	5.88
		E2	3.97	620	0.63	7.75
		E3	3.63	616	0.60	6.72
		E4	4.04	633	0.63	8.02
	Cy9	E1	1.92	504	0.61	2.96
		E2	1.19	513	0.60	1.84
		E3	1.12	504	0.58	1.63
		E4	1.11	521	0.59	1.70
75 mW cm^{-2}	N719	E1	9.41	633	0.66	5.21
		E2	11.81	660	0.59	6.09
		E3	10.23	650	0.61	5.42
		E4	11.45	667	0.61	6.21
	Cy9	E1	5.60	540	0.50	2.01
		E2	3.42	538	0.55	1.35
		E3	3.21	538	0.57	1.31
		E4	3.07	547	0.55	1.24
100 mW cm^{-2}	N719	E1	11.76	640	0.59	4.45
		E2	14.42	660	0.59	5.59
		E3	12.74	660	0.59	4.92
		E4	14.33	676	0.58	5.66
	Cy9	E1	6.81	520	0.48	1.70
		E2	4.42	547	0.53	1.26
		E3	4.09	547	0.55	1.24
		E4	3.83	540	0.55	1.13

6.4 结论

我们选用了一种具有稳定光电性能的菁染料(Cy9)和N719染料作为准固态染料敏化太阳能电池的敏化剂。利用气相法纳米SiO_2对离子液体进行了固化，并通过改变电解质

的成分制备了各种准固态电解质。将它们应用于 DSSCs 而测试了光电化学数据，并对 Cy9 敏化的电池低的光电性能的原因进行了详细的分析。利用 N719 为敏化剂的 DSSCs 在 100 mW cm^{-2} 光强下，得到的最高光电转换效率为 5.66%，短路电流（J_{sc}）、开路电压（V_{oc}）和填充因子（*ff*）分别为 14.33 mA cm^{-2}、676mV 和 0.58。在 1000h 内，对 Cy9 敏化的

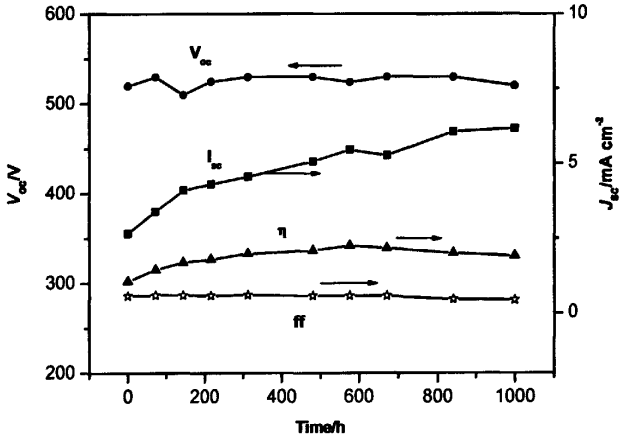


图 6.6 以 Cy9 为敏化剂以 E1 为电解质的 DSSCs 的开路电压(V_{oc})、短路电流(I_{sc})、填充因子(ff)和光电转换效率(η)随时间的变化曲线，测试光强为 75 mW cm^{-2}，光源为 500W 氙灯

Fig. 6.6 Time-course change of open circuit voltage, short circuit current, fill factor and power conversion efficient of device with Cy9 as sensitizer and E1 as electrolyte under irradiation intensity of 75 mW cm^{-2}, white light from a 500W xenon lamp

纳米结构太阳能电池的稳定性进行了测试，结果表明，该电池表现出很好的稳定性。本工作，对光稳定的纯有机敏化剂的设计，准固态染料敏化太阳能电池的进一步研究都有一定的借鉴作用。

第 7 章 其他工作

在这三年的工作中，除了对以上敏化剂及其电解质等系统的研究外，还做了大量的其他敏化剂的表征工作（主要包括器件的制备和优化以及光电化学特性的测试）。以下列出其中的一部分，这里还包括最近以 N719 为敏化剂，使用纳米 SiO_2 固化离子液体取得的最新的进展，以 500W 氙灯为光源，在 100mW cm^{-2} 的光强下，光电转换效率达到 6.44%。

7.1 对四个含羧基的菁染料衍生物的表征

我们课题组尝试把不对称菁染料和香豆素（或其它部分）连接在一起，合成一系列含羧基的菁染料衍生物，研究它们在染料敏化太阳能电池上的性质。结构式如图 7.1 所示。

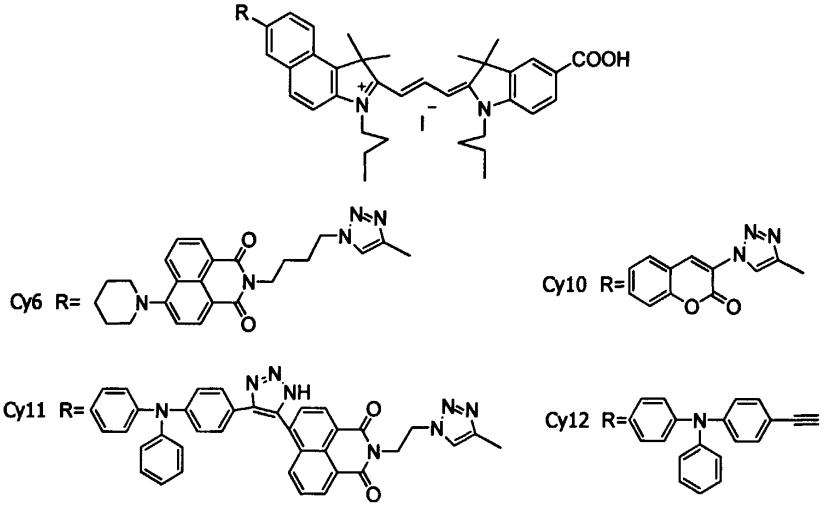


图 7.1 四个不对称菁染料衍生物的结构式

Fig. 7.1 The molecular structures of four asymmetry Cyanine Dyes

由于当时实验条件所限，我们在 20mW cm^{-2} 的光强下，表征了四种染料的光电化学性能。其光电流-电压特性曲线如图 7.2 所示。效果最好的是 Cy12，其光电转换效率达到 8.5%，其短路电流（J_{sc}）、开路电压（V_{oc}）和填充因子（*ff*）分别为 7.13mA cm^{-2}、0.57V 和 0.42。这表明三苯胺在光电转换方面是一非常有效的功能基团。另外，Cy10 的光电效果也不错，四种染料的光电转换数据见表 7.3。

7.2 溴离子菁染料的光电化学性能表征

由于以往我们测试的都是以 I^- 为阴离子的菁染料，后来我们课题组又合成了含有四个羧基的以 Br^- 为阴离子的菁染料（Cy13），其结构式如图 7.3 所示。并对其光电化学性能进行了表征。其光电流-电压曲线如图 7.4。在 75mW cm^{-2} 的光强下，光电转换效率

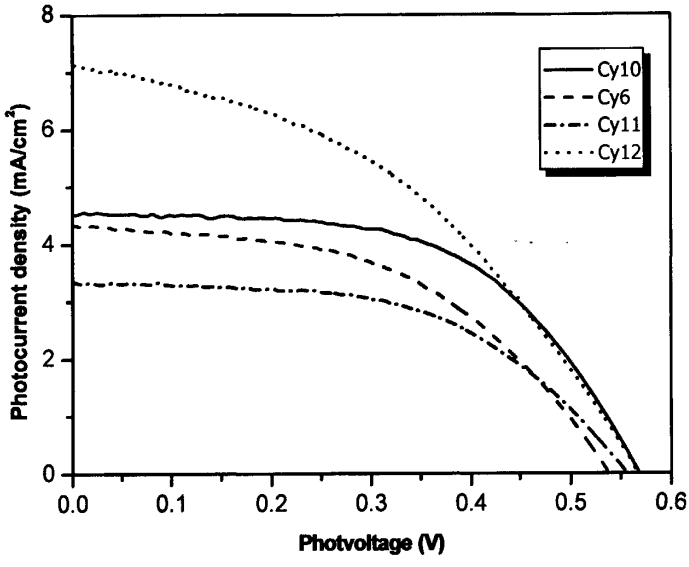


图 7.2 染料 Cy6、Cy10、Cy11 和 Cy12 敏化的二氧化钛纳米多孔膜太阳能电池的电流-电压曲线。

Fig. 7.2 Photocurrent-voltage curve of the TiO_2 electrodes sensitized by Cy6, Cy10, Cy11 and Cy12

表 7.1 染料 Cy6、Cy10、Cy11 和 Cy12 敏化的二氧化钛纳米多孔膜太阳能电池的光电性能

Table 7.1 Properties of solar cells sensitized by Cy6, Cy10, Cy11 and Cy12

染料	J_{sc} (mA/cm^2)	V_{oc} (V)	ff	η (%)	Adsorption (mol·cm^{-2})
Cy6	4.34	0.54	0.49	5.8	2.33×10^{-7}
Cy10	4.55	0.57	0.56	7.3	2.76×10^{-7}
Cy11	3.33	0.56	0.53	5.0	1.76×10^{-7}
Cy12	7.13	0.57	0.42	8.5	2.67×10^{-7}

（η）为 0.84%，其短路电流（J_{sc}）、开路电压（V_{oc}）和填充因子（ff）分别为 2.74mA cm^{-2}、410mV 和 0.56。其光电转换效率较低，不过从其光电流作用谱（图 7.5）可看出，该染料可在 400-700nm 较宽的光谱范围内实现有效的光电转换。

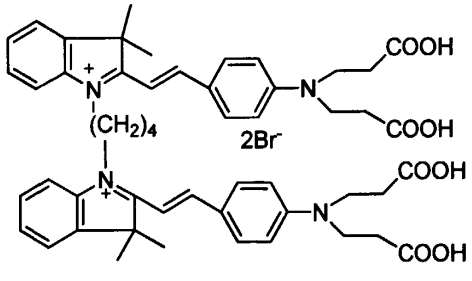


图 7.3 菁染料 Cy13 的结构式

Fig. 7.3 The molecular structure of Cy13.

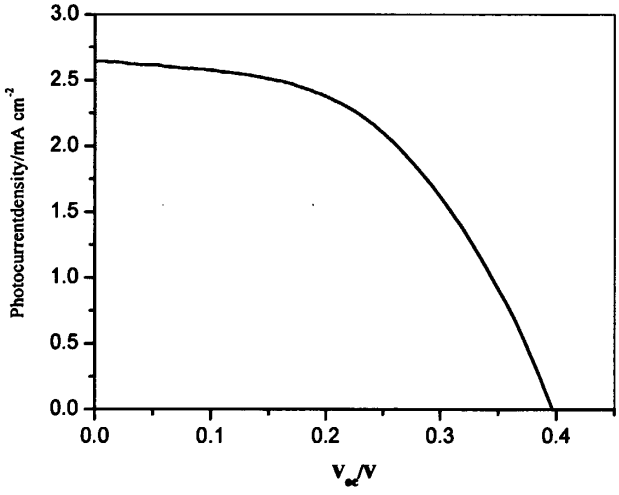


图 7.4 Cy13 敏化的太阳能电池的光电流－电压曲线 (白光光源为 500W 氙灯，光强为 75mW cm^{-2})

Fig. 7.4 Photocurrent-voltage curve of DSSCs sensitized by Cy13, under irradiation intensity of 75mW cm^{-2}

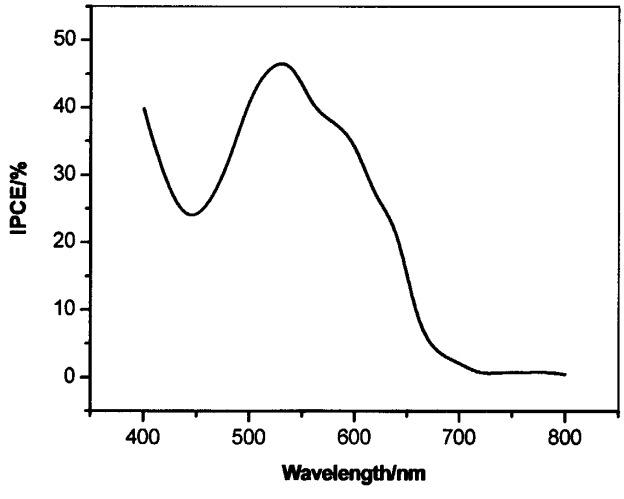


图 7.5 太阳能电池 FTO/TiO_2/Cy13/Pt 的光电流作用谱

Fig. 7.5 Photocurrent action spectra of the solar cell FTO/TiO_2/Cy13/Pt

7.3 苯并噻二唑与三苯胺类染料的光电性能研究

从以前的研究我们得知，三苯胺在染料敏化太阳能电池的敏化剂中是一优秀的电子给体，于是又在以前的工作基础上对其进一步的优化设计，设计出以下两个染料，计为

Cy9 和 Cy14， 其结构式如图 7.6 所示。在 75mW cm^{-2} 的光强下，对其光电性能进行了表征。为了使光电数据具有可比性，我们在同样条件下测试了使用 N719 为敏化剂的 DSSCs，得到了 9.5%的光电转换效率。而我们课题组设计的敏化剂最高的光电转换也达到 7.62%。

图 7.7 给出了两个染料敏化的太阳能电池的光电流作用谱，由图 7.7 可知，两个染料在可见光区 400-700nm 很宽的范围可实现有效的光电转换，最高 IPCE 值超过 80%。图 7.8 为两个染料敏化的太阳能电池的光电压-电流特性曲线。比较图 7.7 和图 7.8，可以看出 IPCE 和 I-V 曲线具有一定的对应关系。由图 7.8 得出的光电数据以及 N719 在该条件下的测试结果列于表 7.2。

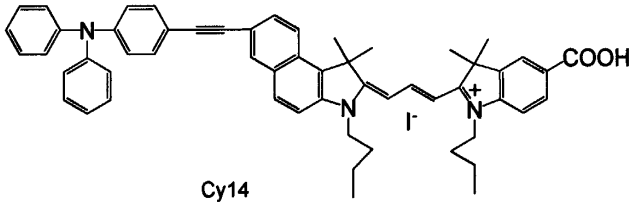


图 7.6 菁染料 Cy14 的分子结构式

Fig. 7.6 Molecular structure of cyanine dyes Cy14

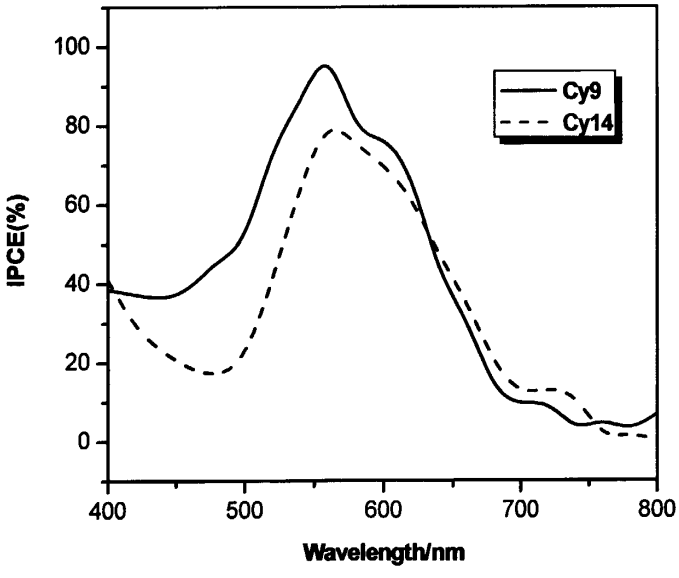


图 7.7 菁染料(Cy9 和 Cy14)敏化的纳米晶 TiO_2 电极的光电流作用谱

Fig. 7.7 Photocurrent action spectra of the TiO_2 electrodes sensitized by Cy9 and Cy14

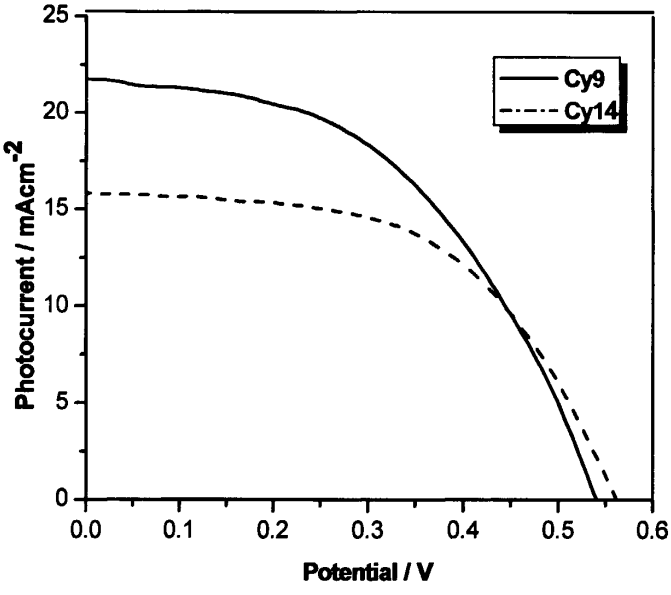


图 7.8 染料(Cy9 和 Cy14)敏化的纳米晶 TiO_2 电极在 75 mW cm^{-2} 光强下的光电压-电流特性曲线

Fig. 7.8 Photocurrent-voltage curve of Cy9 and Cy14 sensitized TiO_2 electrodes under 75 mW cm^{-2} light intensities.

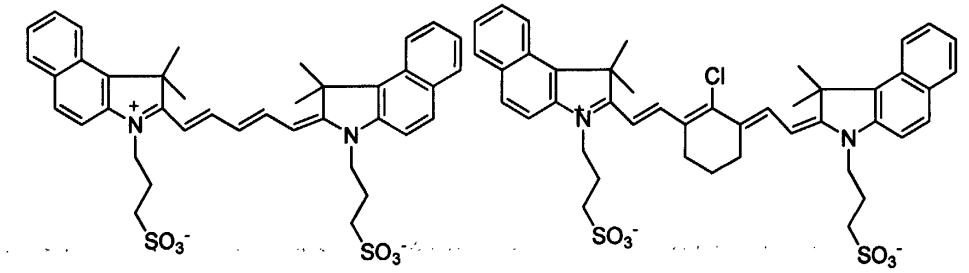
表 7.2 染料(Cy9 和 Cy14)和 N719 敏化的太阳能电池的光电性能参数

Table 7.2. Performances of dyes（Cy9 and Cy14）and N719 sensitized solar cell

Dye	J_{sc} (mAcm^{-2})	V_{oc} (V)	*ff*	η (%)
Cy9	22.10	0.54	0.48	7.62
Cy14	15.79	0.57	0.55	6.58
N719	27.25	0.64	0.41	9.50

7.4 两个磺酸基敏化剂的光电化学表征

我们课题组以前的工作一直集中在羧酸基的敏化剂，后来我们又合成了两个磺酸基敏化剂。研究表明，从器件的表面颜色可以看出磺酸基团的吸附能力没有羧酸基强。故而导致非常低的光电效率。其中 Cy15 较 Cy16 好，在 100mW cm^{-2} 的光强下光电转换效率为 0.27%，其短路电流（J_{sc}）、开路电压（V_{oc}）和填充因子（*ff*）分别为 0.95mA cm^{-2}、0.41V 和 0.70。从图 7.10 和表 7.3 可以看出，虽然 Cy15 敏化的太阳能电池总的光电转换效率低，但其填充因子非常高，达到 0.70。Cy16 敏化的电池的短路电流较 Cy15 高一点，但由于总体性能较差而导致总的光电转换效率更低。就这两个染料而言，可能是 Cy16 中间的 Cl 取代基的吸电子能力较强而使电子的传输能力下降而导致总体的光电转换效率下降的。磺酸基敏化剂还有待于从敏化剂结构及其器件的角度进一步优化，提高短路电流和开路电压，这样可以使其总的光电转换效率提高。



Cy15 Cy16

图 7.9 染料 Cy15 和 Cy16 的结构图

Fig. 7.9 The molecular structures of two dyes of Cy15 and Cy16

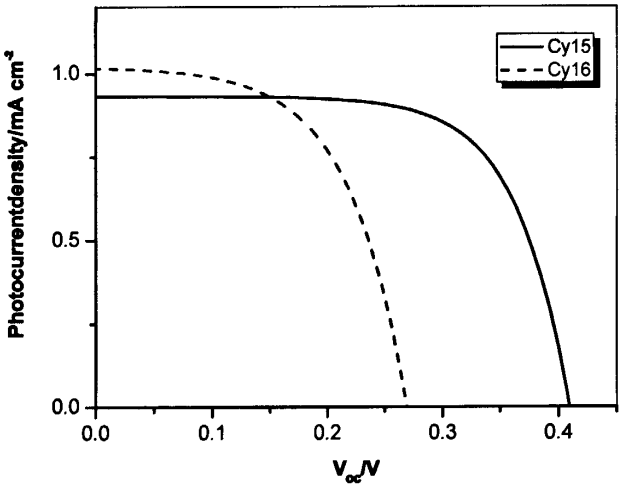


图 7.10 染料 Cy15 和 Cy16 敏化的纳米晶 TiO_2 电极在 100 mW cm^{-2} 光强下的光电压-电流特性曲线

Fig. 7.10 Photocurrent-voltage curve of Cy15 and Cy16 sensitized TiO_2 electrodes under 100 mW cm^{-2} light intensities.

表 7.3 染料 Cy15 和 Cy16 敏化的二氧化钛纳米多孔膜太阳能电池的性能

Table 7.3 Properties of solar cells sensitized by Cy15 and Cy16

染料	J_{sc} (mA/cm^2)	V_{oc} (V)	ff	η (%)
Cy15	0.95	0.41	0.70	0.27
Cy16	1.02	0.27	0.64	0.18

7.5 N719 为敏化剂的准固态 DSSCs 的研究新进展

第 6 章我们使用气相法纳米 SiO_2 R974 来固化 1-丁基-3-甲基咪唑碘（MBII）用于 N719 敏化的 DSSCs 中，取得了不错的结果。后来我们制备了 1-丙基-3-甲基咪唑碘（MPII），由于这种纳米二氧化硅是疏水性的，对于烷基链较短的离子液体很难固化。

非常感谢德固赛公司又为我们提供了亲水性的纳米二氧化硅 Aerosil 200。改变了二氧化硅的表面特性，对于准固态电解质的制备过程影响特别明显。由于离子液体的极性特别大，所以用亲水性的 SiO_2 非常容易固化。另外我们又从器件的角度考虑，由于准固态电解质的离子传输速率较小，减小两个电极间的距离，可以提高染料氧化态的还原速率，很可能使电池的光电性能得到改善。我们使用的电解质的组成为：0.5M I_2、0.1M 硫氰酸胍的 MPII 溶液，以 5wt%的气相法纳米 SiO_2 Aerosil 200 固化。图 7.11 为该准固态电池的 I-V 特性曲线，由图 7.11 可知，在 100mW cm^{-2} 的白光照射下，短路电流为 20.81mA cm^{-2}、开路电压为 603mV、填充因子为 0.51，总的的光电转换效率达到 6.44%。

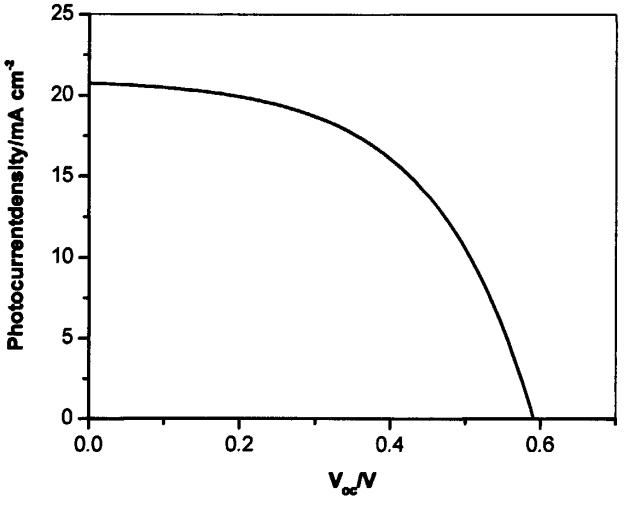


图 7.11 N719 敏化的准固态染料敏化太阳能电池在 100 mW cm^{-2} 光强下的光电压-电流特性曲线

Fig. 7.11 Photocurrent-voltage curve of N719 sensitized DSSCs with quasi-solid state electrolyte under 100 mW cm^{-2} light intensities.

7.6 总结和展望

可喜的是，我们不光是在器件的制备方面积累了大量的经验。也在敏化剂的结构设计、优化等方面取得了很多很好的经验。最近，我们又在准固态染料敏化太阳能电池方面取得了一定的突破。有望通过进一步改善器件结构和电解质成分使总的光电转换效率进一步提高。最终我们的目标是在全固态染料敏化太阳能电池上有所突破。

第 8 章 结论

本文从选择新的敏化剂和对染料敏化太阳能电池的电解质固化两方面进行了系统的研究。不仅研究了敏化剂的结构对电池的光电性能的影响，还利用染料间吸收光谱在可见光区的互补性研究了染料敏化太阳能电池的共敏化。在电解质方面，利用纳米 SiO_2 对离子液体进行了成功固化，使 N719 敏化的准固态太阳能电池的光电转换效率在 $100mWcm^{-2}$ 的光强的白光照射下达到 6%左右。归纳本文的实验结果可得出以下结论：

1. 利用三个具有不同长度碳链取代的半菁类染料 2-{2-[4-(N,N-二羧乙基氨基)苯基]乙烯基}-1,3,3-三甲基-3H-吲哚碘盐(Cy1), 2-{2-[4-(N,N-二羧乙基氨基)苯基]乙烯基}-1,1-二甲基-3-丁基-3H-吲哚碘盐(Cy2)和 2-{2-[4-(N,N-二羧乙基氨基)苯基]乙烯基}-1,1-二甲基-3-辛基-3H-吲哚碘盐(Cy3)敏化太阳能电池，并研究了它们的的光电化学性能。其中 Cy1 的敏化效果最好，在 $100mW/cm^2$ 氙灯光源下，开路电压、短路电流、填充因子和转换效率分别是 430mV、$1.31mA/cm^2$ 、0.52、0.29 %。研究表明，随着半菁染料碳链取代基的增长，转换效率逐渐降低。

2. 以三个新型菁染料 2-[(1-丁基-3, 3-二甲基-5-羧基-二氢吲哚)丙烯基]-[1-丁基-3,3-二甲基-7-(1-乙基-1,2,3-三唑]-苯并吲哚碘（Cy4）、2-[(1-丁基-3,3-二甲基-5-羧基- 二氢吲哚)丙烯基]-{1-丁基-3,3-二甲基-7-[(4-哌啶-*N*-乙基-1,8 –萘酰亚胺)- 1,2,3-三唑]}-苯并吲哚碘（Cy5）、2-[(1-丁基-3,3-二甲基-5-羧基- 二氢吲哚)丙烯基]-{1-丁基-3,3-二甲基-7-[(4-哌啶-*N*-丁基-1,8 –萘酰亚胺)- 1,2,3-三唑]}-苯并吲哚碘（Cy6）为敏化剂研究了它们的光电化学性质与结构的关系。吸附在 TiO_2 电极上的吸收光谱与它们在溶液中的吸收光谱相比较，均同时发生蓝移和红移。Cy5 和 Cy6 由于含有萘酰亚胺基团，使它们较 Cy4 具有更强更宽的吸收，实验结果表明，它们具有更好的光电转换性能。以氙灯为光源，在 $75mW\ cm^{-2}$ 光强下，Cy6 的光电转换效率最高为 4.80% (J_{sc} = 14.5 mA cm^{-2}, V_{oc} = 500 mV, FF = 0.49)。

3. 由于两个羧基菁染料 2-[(1-丁基-3,3-二甲基-5-羧基- 二氢吲哚)丙烯基]-{1-丁基-3,3-二甲基-7-[(4-哌啶-*N*-乙基-1,8-萘酰亚胺)-1,2,3-三唑]} –苯并吲哚碘(Cy5)和 1-丁基-2-[(1-丁基-3,3-二甲基-二氢吲哚)(1,3-二戊烯)]-3,3-二甲基-6-羧基-吲哚碘(Cy7)的紫外－可见吸收光谱在可见光区具有互补性，我们尝试了将这两种染料用于染料敏化太阳能电池的共敏化研究。分别以 Cy5、Cy7 和它们的混合物作为纳米晶 TiO_2 太阳能电池的敏化剂。研究表明 C31 (摩尔比:Cy5:Cy7=3:1)敏化的太阳能电池在 100 mW cm^{-2} 和 20 mW cm^{-2} 的白光照射下分别产生了最高的光电效率 3.84% 和 6.10%，这表明共敏化是提高染料敏化太阳能电池光电转换效率的有效手段。

4. 利用炭黑-聚苯胺的复合物 (PACB)与 1-甲基-3-丙基咪唑碘(MPII)制备了一种全新的固态电解质，并用于一个新的菁染料 7-{1-[2-(4-对氧氮己烷-1,8-萘酰亚胺)乙基]- 1,2,3-三唑-4-}-2-[3-(5-羧基-3,3-二甲基-1-丁基-二氢吲哚- 2-亚甲基)-丙烯基]-1,1-二甲基-3-丁

基-苯并吲哚碘(Cy8)敏化的染料敏化太阳能电池，进行了光电化学研究。在 20 mW/cm^2 光强的白光照射下，得到的总的光电转换效率为 0.7%，短路电流(J_{sc})、开路电压(V_{oc})和填充因子(*ff*)分别为 0.44 mA/cm^2、 550mV 和 0.58，光源为 500W 氙灯。该固态电解质的最大优点为不挥发，不易燃，用于 DSSCs 容易封装。

5. 利用气相法纳米 SiO_2 对离子液体进行了成功的固化，并通过改变电解质的成分，制成各种准固态电解质。我们选用了一种具有稳定光电特性的菁染料(Cy9)和 N719 染料作为准固态染料敏化太阳能电池的敏化剂。将各种准固态电解质用于这两种敏化剂敏化的太阳能电池中测试了它们的光电化学数据并详细的分析了 Cy9 敏化的太阳能电池光电转换效率较低的原因。由 N719 敏化的准固态 DSSCs 在 100mW cm^{-2} 的光强下，得到的最高光电转换效率为 5.66%，短路电流 (J_{sc})、开路电压 (V_{oc}) 和填充因子 (*ff*) 分别为 14.33 mA cm^{-2}、676mV 和 0.58。在 1000h 内，测试了 Cy9 敏化的纳米结构太阳能电池的稳定性，结果表明，该电池表现出很好的稳定性。本工作，对光稳定的纯有机敏化剂的设计，准固态染料敏化太阳能电池的进一步研究都有一定的借鉴作用。

6. 除了以上对敏化剂和电解质的系统研究外，在实验过程中还表征了大量的全新敏化剂，这里列出的只是其中的一部分。其中也有效率较高的敏化剂比如 7.3 中的染料 Cy9。值得一提的是使用纳米二氧化硅 Aerosil 200 使 N719 敏化的太阳能电池效率在 100mW cm^{-2} 光强的白光照射下接近 6.5%。

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致谢

当博士论文即将画上一个句号的时候，回顾这三年的工作，有辛勤工作的汗水也有实验成功时激动的泪水。是我的导师田禾教授不断的用最前沿的知识武装我的头脑并指引我前进的。在田老师的指导下，我不但在实验技能方面取得了一定的进展，最重要的是学会了独立思考和独立工作的能力，这对于我将终身受益。在这里对田老师表示由衷的感谢和崇高的敬意。也感谢花建丽老师、朱为宏老师、孟凡顺老师在我的科研工作最需要帮助的时候伸出了援助之手。感谢硕士生金樱华在敏化剂和离子液体的制备方面给予的大量帮助。感谢博士生马学美和已毕业的詹文海博士为我提供敏化剂。感谢博士生张琼，刘博和宁志军在实验过程中给予的帮助。感谢复旦大学李富友教授，杨红博士在太阳能电池的制备和测试方面给予的探讨和帮助。

也感谢我的父母和我的妻子孟凡云在背后默默无闻的奉献和对我的工作的大力支持。

再一次对所有帮助过我的人表示感谢。