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Room-Temperature Liquid Dyes

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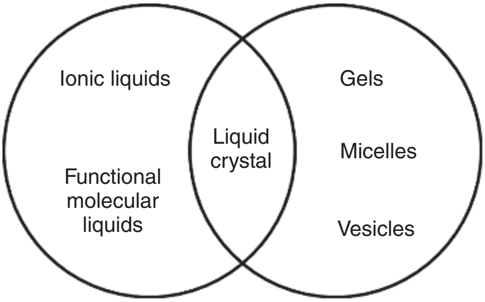
1.1 Introduction

Optoelectronically active functional molecules derived from π-conjugated chromophores [1] are becoming increasingly desirable. Their flexibility, light weight, processability, and low cost of fabrication provide them with an advantage over their inorganic counterparts, which are intrinsically hard and have no deformability [2]. The tailorable chemical functionalization on the π-conjugated unit, leading to tunable properties, makes them suitable for various applications in the field of optoelectronics [3]. Due to the strong π–π interactions between the π-conjugated units, these molecules generally exist as solids. As solids cannot be directly fabricated on the devices, they are either dissolved in organic solvents and coated onto a substrate, or used as gels [4] or as self-assembled phases [5]. They have been also applied as interfacial films. However, defect-free fabrications and homeotropic alignments are rather difficult due to the strong ordering and tendency to crystallize. The most common soft materials in this regard are liquid-crystalline (LC) materials. LCs are mesophases existing between the crystalline and isotropic phases [6]. As LC materials exhibit long-range order (micrometer scale), they are advantageous over locally ordered nanomaterials. However, LC phases only form on a special class of molecules and can be either thermotropic or lyotropic. They need the assistance of temperature/solvent to exhibit their properties different from that of the intrinsic chromophores in the monomeric form. Thus, simple prediction of material properties from LCs is almost impossible, and deep investigation is needed in holding the perfectly ordered state.

A clever strategy to retain the intrinsic characteristics of the chromophore, more often in the monomeric form, in a solvent-free paradigm is by designing functional molecular liquids (FMLs) [7]. FMLs are uncharged, solvent-free liquids at room temperature and can be categorized as one of the organic soft materials (Scheme 1.1). A close-knit member in the family is the class of "ionic

Functional Organic Liquids, First Edition. Edited by Takashi Nakanishi.



Scheme 1.1 Venn diagram representation of organic soft materials.

liquids" [8]. Ionic liquids, which are molten salts at a relatively low temperature (below 100 °C), result from weak ionic interaction and comprise bulky cationic and anionic counterparts [9]. They possess many useful properties, such as low volatility, low melting point, noninflammability, high thermal stability, and ionic conductivity. They have mainly been explored as solvents for carrying out reactions and as catalysts, and the recent trend of their utilization is in battery research.

FMLs are easily processable due to their fluidic nature and are environment friendly, as they do not require solvents in further fabrications and are nonvolatile. As most studied systems are based on chromophores, these liquids possess luminescent properties. Tunable emission and facile incorporation of other emissive materials into the liquid matrix have led to a deep understanding of phenomena such as excited-state energy transfer and white light emission. They are desired in the isotropic phase; however, interchromophoric (π–π) interactions may lead to local ordering, equipping them with properties such as liquid crystallinity at lower temperatures. This chapter discusses the strategy of designing room-temperature FMLs and gives detailed insights into the applications of these materials developed so far.

1.2 Design Strategy: Alkyl Chain Engineering

Organic molecules and polymers containing π-conjugated backbones are widely used in organic/polymeric optoelectronic devices by virtue of their suitable optical, semiconducting, and electronic properties. However, in general, these π-conjugated substances tend to exist as solids at room temperature due to the strong π–π interactions. Although conventional solution-processing techniques such as spin coating and solvent-assisted methods have been used for fabrication of ordered films, few molecules form poorly soluble random aggregates. This makes the rich semiconducting π-conjugated moieties unsuitable for showing proper optoelectronic performances such as charge transport. Furthermore, aerial oxidation and photooxidation have often been reported to cause photodimerization/polymerization, resulting in the loss of the semiconducting property of the π-conjugated backbone.

A simple synthetic technique to address the aforementioned challenges is to attach solubilizing linear or branched alkyl chains [10]. The introduction of flexible and bulky alkyl chains on the functional π-conjugated units gives us a tool for fine-tuning the balance between π–π interactions among neighboring chromophores and van der Waals (vdW) interactions governed by the attached alkyl chains. This technique not only softens the intrinsically rigid π-molecular-based material but also allows for unique phase transition ranging from solids to thermotropic LC to room-temperature liquids. Furthermore, the bulky alkyl chains can wrap/cover the π-conjugated units, preventing them from aerial oxidation/or photodimerization/polymerization, and thus can guarantee them a longer lifetime with their advanced functions.

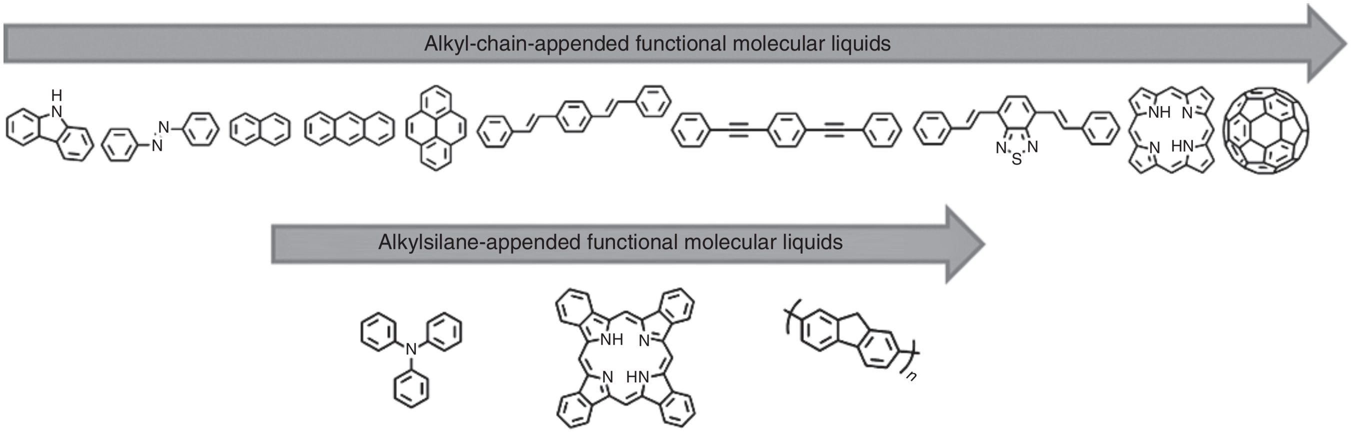
The detailed discussions of the organic liquid dyes presented in the following sections have been organized in the order of the size of their functional cores (Scheme 1.2).

1.3 Alkylated π-Molecular Liquids

Substitution of multiple linear or branched alkyl chains has dramatically led to the phase transformation in many π-conjugated systems. This has made them useful for solvent-free direct applications in optoelectronics. In this section, the impact of the alkyl chain substitution on the phase behavior of several π-conjugated molecular systems has been briefly discussed. This section presents a detailed account of room-temperature FMLs. It covers the aspects of the synthetic strategies adopted to tune the physical properties of FMLs. An attempt is made to cover the development of these functional materials so far and the advances made in deriving functions from them.

1.3.1 Carbazoles

The first reported liquid carbazoles applied in an application was from the group of Peyghambarian and coworkers. 9-(2-ethylhexyl)carbazole (**1**, Figure 1.1a), the room-temperature liquid, was utilized as the solvent in ellipsometry measurements for determining the birefringence induced by electric field in photorefractive polymer composites [12]. Further insights into the charge-transport properties of **1** were provided by the research group of Wada and coworkers [13]. They demonstrated **1** to be a p-type semiconductor and determined the drift hole mobility by time of flight (TOF) method to be 4×10^{-6} cm^2 V^{-1} s^{-1}. Liquid carbazoles have more recently been employed as the liquid-emitting layer of organic light-emitting diodes (OLEDs) [14]. The liquid host **1** was used along with 6-(1)-naphthalene-2-carboxylic acid hexyl ester (BAPTNCE) as the guest emitter and tetrabutylammonium hexafluorophosphate (TBAHFP) as the electrolyte. Using a liquid emitter had two major advantages over conventional OLEDs. Firstly, the liquid-emitting layer and the electrodes do not lose contact upon significant bending of the device. Secondly, the liquid emitters that degraded in the OLED can be easily replenished by



Scheme 1.2 Functional π-conjugated molecular units organized according to ascending size, as discussed in this chapter. These functional π-units have been appended with alkyl chains (from left to right; carbazole, azobenzene, naphthalene, anthracene, pyrene, oligo-(*p*-phenylenevinylene), oligo-(*p*-phenyleneethylene), benzothiadiazole, porphyrin and C_{60} fullerene) or alkylsilane chains (from left to right; triarylamine, phthalocyanine, and oligofluorene) to develop functional liquid dyes at ambient temperature.

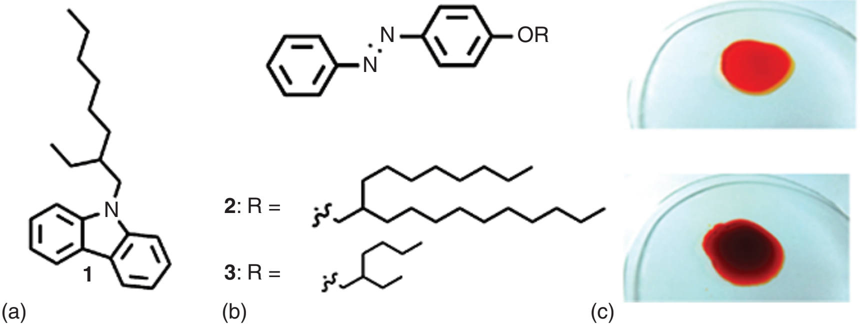


Figure 1.1 Chemical structures of (a) liquid carbazole **1** and (b) liquid azobenzenes **2** and **3**. (c) Photographs of the trans (orange, upper) and the cis state (deep red, bottom) conformations of **3** upon irradiation with UV at 365 nm. Source: Adapted with permission from Masutani et al. [11] Copyright 2014, Royal Society of Chemistry.

a fresh flow of the liquid, thus increasing the lifetime of the OLED over the existing ones in the device developed by Adachi and coworkers. The maximum external electroluminescence quantum yield (Φ_{EL}) achieved is 0.31 ± 0.07%, and the maximum luminance achieved is approximately 100 cd m^{-2}. The Φ_{EL} and the maximum luminance are 10 and 100 times, respectively, higher than the OLEDs reported so far. Thus, examples of this kind are advantageous over the conventionally applied materials in optoelectronic devices.

In addition, in the device developed by Adachi and coworkers, liquid carbazoles were employed to create liquid organic distributed feedback lasers built on flexible corrugated polymeric patterns [15]. **1** was used as a host matrix on which the blue-, green-, and red-emitting laser dyes were added. Cascade energy transfer between the chromophores efficiently channelized the lasing wavelength to cause a broad spectrum over the visible color range.

1.3.2 Azobenzenes

An interesting example of liquefaction of azobenzenes was demonstrated by Akiyama and Yoshida [16]. The design strategy was functionalizing a sugar alcohol scaffold with multiple azobenzene chromophores. When the azobenzenes were in the trans form, they were yellow crystalline solids. However, photoisomerization by UV light to the cis form resulted in the liquid state. Among a series of multiple azobenzene-arm-appended sugar scaffolds, the ones having an LC transition could be reversibly switched back to the trans state upon irradiation with visible light. However, the conversion to the cis form was a pure photochemical transformation, as the transition occurred even at room temperature. The cis-formed liquids were stable for at least half a day at room temperature. In this strategy, the sugar backbone acts as the flexible moiety. The liquids were cleverly employed as reusable adhesives and were demonstrated for sealing and detaching two quartz plates upon photoirradiation.

Our group had synthesized a liquid azobenzene by attaching a 2-octyldodecyl chain (**2**, Figure 1.1b) [17]. As we had observed directed self-assembly in the case of alkylated fullerenes (see Chapter 9), we desired to extend the concept of “hydrophobic amphiphile” with a smaller π-conjugated core. **2** served the purpose and showed a directed structural formation of micelles with an assist of alkane solvents.

An interesting application of a liquid azobenzene derivative has been demonstrated by Kimizuka and coworkers [11]. They employed an azobenzene carrying a 2-ethylhexyl chain (**3**, Figure 1.1b) as a solar thermal fuel. The trans-to-cis conversion has been extensively used for molecular switches and has been mainly performed in solid azobenzenes. However, employing trans-to-cis photoisomerization for storage of photon energy had been unsuccessful because such a phenomenon was suppressed in the condensed phase. The trans-to-cis conversion of compound **3** was performed upon photoirradiation with an ultrahigh-pressure mercury lamp at 365 nm (Figure 1.1c). High energy density was obtained in the process.

1.3.3 Naphthalenes

Preceeded by benzene, naphthalene is the smallest π-conjugated chromophore. As the absorption and emission features of naphthalenes can be conveniently probed using conventional techniques, this small dye unit was employed to create functional liquids with monomer-rich luminescence properties [18].

By a simple and effective alkylation strategy, 1- and 2-alkylated naphthalenes were synthesized. The regioisomeric alkylated naphthalenes were found to exist as liquids of very low complex viscosity (η^* in the range of 38.4–67.0 mPa s at 25 °C [$\omega = 10\,\text{rad}\,\text{s}^{-1}$]). Detailed optical investigations indicated the existence of excimeric state in 1-naphthalenes in the solvent-free state, whereas the 2-substituted regioisomers were found to be monomeric in nature. This simple design strategy serves as a guideline for synthesizing novel alkylated π-molecular liquids with predictable properties.

1.3.4 Anthracenes

Anthracenes, being the smallest member of the acene family, are well-sought out candidates for photosensitizer and organic laser dyes. Their blue emission and high quantum yield are the most attractive features. However, they are highly sensitive to light (dimerization) and air (oxidation) and highly crystalline. Therefore, fabricating uniform films from anthracenes for devices with long-term stability poses a grave challenge. Alkyl chain engineering on the anthracene unit has been able to address this issue effectively [19]. Functionalizing the anthracene unit with multiple branched alkyl chains has led to nonvolatile, blue-emitting, uncharged organic liquids that retain the intrinsic monomeric optical properties (Figure 1.2a,d). The wrapping of the alkyl chains on the anthracene unit can hamper the intermolecular π–π (anthracene–anthracene) interactions and provides better protection from atmospheric oxygen. This makes them more stable than their unsubstituted crystalline counterparts. While **4** was stable for 15 hours in a dilute dichloromethane solution and for 4 hours in the neat state under photoirradiation (365 nm, 100 W m^{-2}, Xe lamp), the unsubstituted

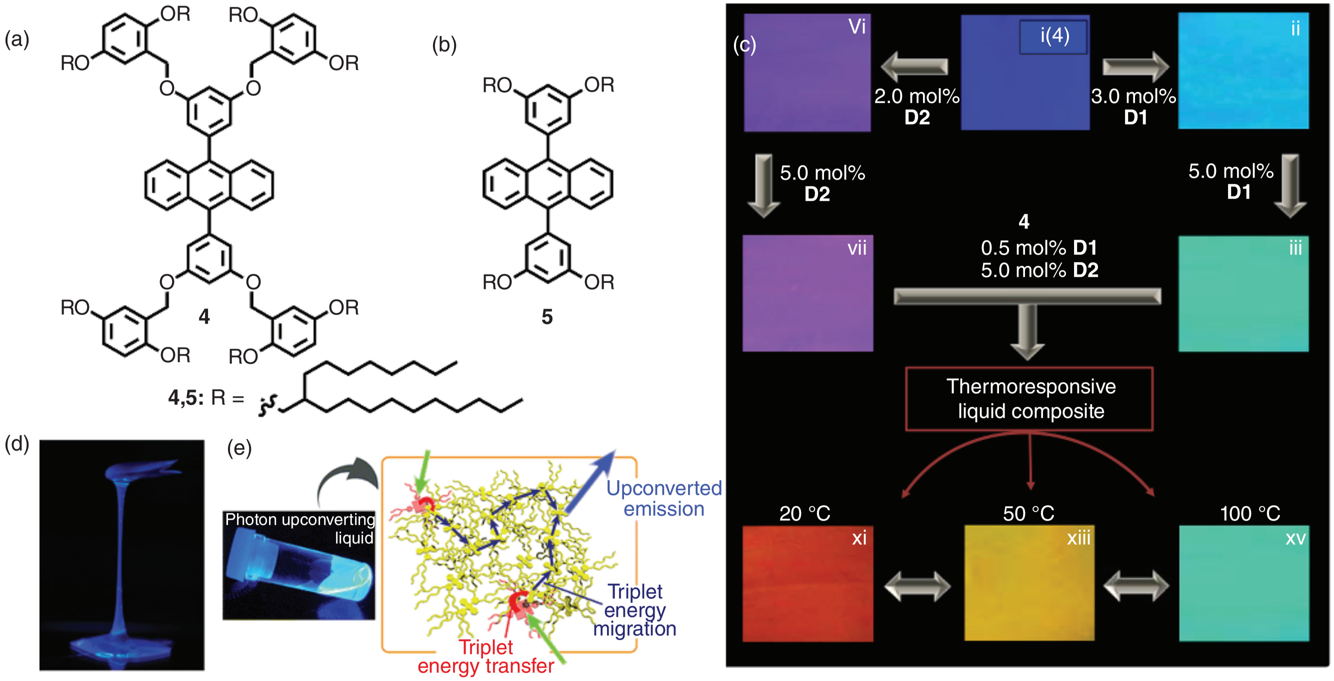


Figure 1.2 (a,b) Chemical structures of liquid anthracenes **4** and **5**; (c) photographs demonstrating the emission color tunability and thermoresponsiveness of the composites of **4**, **D1** (0.5 mol%) and **D2** (5 mol%); (d) photograph of solvent-free state of **4** under UV at 365-nm irradiation; (e) schematic of the photon upconversion system created by utilizing a liquid anthracene **5**. Source: Reproduced with permission from Babu et al. [19]. Copyright 2013, Macmillan Publishers Limited and adapted with permission from Duan et al. [20]. Copyright 2013, American Chemical Society.

anthracene started its decomposition after only 2 hours. Here, it is noted that there are no photodimerization reactions, but still its 9,10-endoperoxides are formed. Furthermore, the fluorescence quantum yields of the liquid anthracenes were around 55% in solvent-free neat state under ambient conditions. An alternative utilization of the highly blue emissive donor liquid was made by blending them with minute amounts of acceptor molecules and tuning their emission color through energy transfer (Figure 1.2c). Tunable luminescence was achieved by blending solid dopants 9,10-bis(phenylethynyl)anthracene (**D1**) and tris(1,3-diphenyl-1,3-propanedionato)(1,10-phenanthroline)europium (III) (**D2**) in minute amounts. The incorporation of incremental amounts of acceptor **D1** led to color tuning from blue to yellow at a single blue light excitation. This is because of the quenching of donor emission and the emergence of the emission of the acceptor and fluorescence resonance energy transfer (FRET) mechanism. The donor–acceptor composite was further made thermoresponsive by blending in **D2**. Incremental percentages of **D2** (2–5 mol%) in **4** tuned the color from violet to purple, due to weak energy transfer. A tricomponent mixture consisting of **4**, **D1** (0.5 mol%), and **D2** (5 mol%) resulted in a red emission. Due to the thermoresponsiveness of **D2**, heating the tricomponent mixture from room temperature to 50 °C resulted in yellow emission. A further increase in temperature led to quench the **D2**'s red emission and display emerald green emission, mainly contributed from **D1**'s emission. Therefore, a system of fluorescent thermometer was successfully constructed from composites of alkylated anthracenes.

Another interesting demonstration of the utilization of liquid anthracene **5** was made by Kimizuka and coworkers (Figure 1.2b,e). They successfully employed liquid **5** as an acceptor in an upconversion luminescent system [20]. Efficient upconversion systems known so far have been achieved in solution as the diffusion of the triplet molecules is a prime requisite. However, the volatility of organic solvents and deactivation of triplet state caused by molecular oxygen pose serious challenges. Harvesting the fluidic nature of **5** and its photostability due to shielding by multiple alkyl chains could address this issue. An alkyl-chain-substituted Pt(II) porphyrin derivative was chosen as the donor (sensitizer) which was highly miscible with liquid **5**, the blue emissive acceptor. An upconversion quantum efficiency of around 28% was achieved in solvent-free organic liquid system under ambient conditions, without matrix. It should be noted that the liquid **5** formed a liquid state, but in fact it was in a metastable supercooled liquid state [21]. Mixing with the alkyl-chain-substituted Pt(II) porphyrin derivative might secure its liquid form in their study.

1.3.5 Pyrenes

Adachi and coworkers synthesized a liquid pyrene **6** and used it as the emitting material in OLED (Figure 1.3a) [15]. The most important property of the OLED was its fast emission recovery because the liquid pyrene could be replenished as soon as it was consumed in the device. The design involved a mesh-structured cathode made of aluminum in which the liquid material could fill smoothly and uniformly, leading to the OLED having emission over a large area. A back reservoir enabled the injection of the liquid emitter through the cathode into the gap

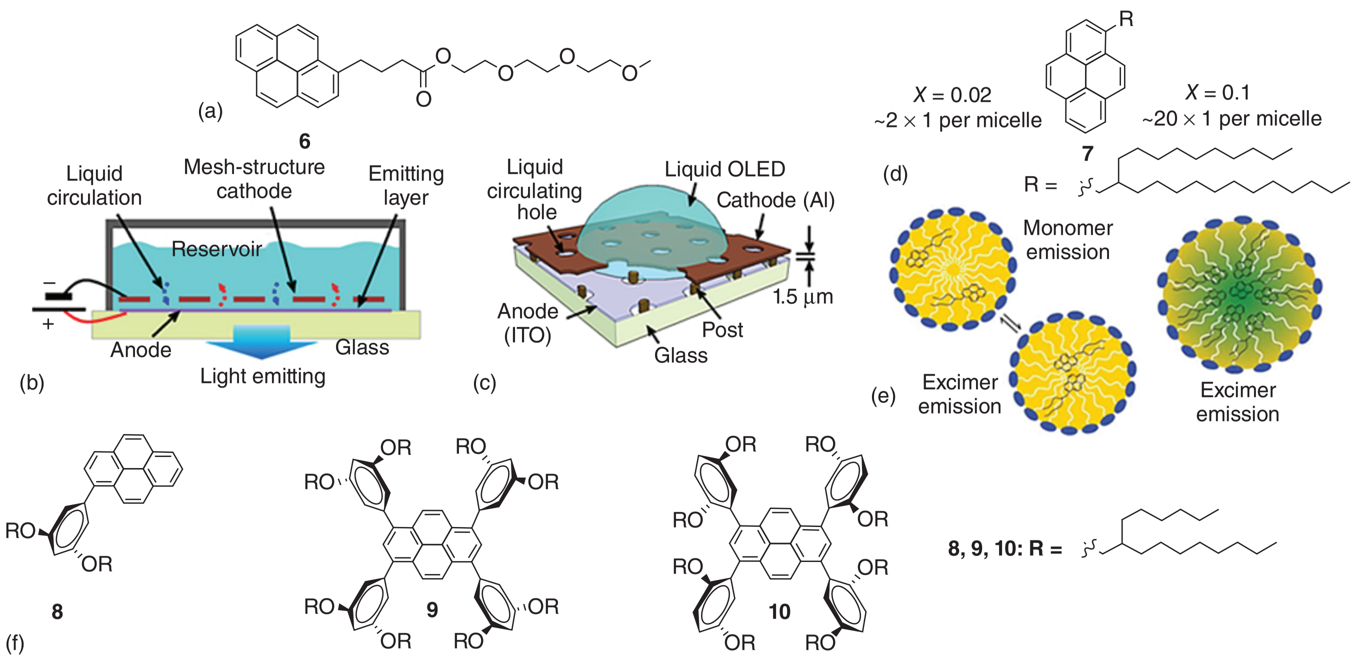


Figure 1.3 Liquid pyrenes: (a) **6** reported by Adachi and coworkers and employed in OLED; (b,c) show schematic representation and device structure made by microelectromechanical system (MEMS) processing; (d) an alkylated pyrene (**7**) reported by Hollamby and coworkers; (e) luminescent micellar structures formed from **7**; (f) alkylated pyrenes (**8**–**10**) with varied alkyl chain number and position of substitution that serve as a guide for molecular design of alkyl-π liquid dyes. Source: Adapted with permission from Shim et al. [15]. Copyright 2012, AIP Publishing LLC and reproduced with permission from Hollamby et al. [22]. Copyright 2016, Royal Society of Chemistry.

between the electrodes, thus causing convection circulation (Figure 1.3b,c). The external electroluminescence quantum efficiency (EQE) of the device was found to be 0.2%. This unique OLED structure has prospects in creating uniform and degradation-free lighting devices.

Hollamby and coworkers reported an excimeric-fluorescent liquid pyrene derivative **7** (Figure 1.3d) with a high fluorescence quantum yield in the solvent-free state (65%) [22]. The authors prepared stable oil-in-water emulsions with the liquid pyrene as the oil phase. Detailed structural investigations were carried out by small-angle neutron scattering (SANS). The SANS analysis revealed a cylindrical micellar structure with the microemulsions behaving as hard spheres at intermediate oil loading. Interestingly, the emission of the microemulsions could be tuned by the droplet size (Figure 1.3e). Taki et al. recently reported trialkyl-substituted pyrene liquids and their formation of color-tunable nanoparticles [23].

Although the field of FMLs is rapidly developing, there is no clear rationale for designing the molecule to extract the desired function. Our group has recently exploited the dual monomer–excimer fluorescence of liquid pyrenes to clearly lay down a guidance for molecular nanoarchitectonics [24]. We synthesized a series of alkylated pyrene liquids (**8**–**10**), which have branched alkyl chains of different substitution patterns and employed them as a rational FML model (Figure 1.3f). The number and substitution motif of the alkyl chain on the pyrene unit was modulated to create a series of derivatives that exhibit emission from the excimer to an uncommon intermediate to the monomer. The pyrene moiety was effectively isolated by wrapping of alkyl chains in the case of compound **10**, showing its monomer emission. While the pyrene moiety is only partially covered by the alkyl chains, i.e. **8**, its luminescence has a strong excimer feature. Thus, a direct correlation between the molecular structure and the π–π interactions was established by detailed investigation of liquid pyrenes.

1.3.6 π-Conjugated Oligomers

A few rod-shaped π-conjugated oligomers were substituted with branched alkyl chains and studied as luminescent solvent-free liquids at room temperature. A few of them were exploited as the donor matrix for acceptor dopant molecules and detailed investigations of energy transfer phenomenon were carried out. These are described here.

1.3.6.1 Oligo-(*p*-phenylenevinylene)s (OPVs)

Liquid oligo-(*p*-phenylenevinylene)s (OPV)s (**11–14**, Figure 1.4a) were synthesized by attaching branched alkyl chains to two different OPV cores [25]. OPVs have remarkable fluorescent blue emission characteristics, high stability, and self-assembling tendencies. It is, therefore, a good choice of chromophore for optoelectronics and is widely explored in this field. The liquid OPVs (**11**–**14**) were determined to have low viscosities ranging from 0.64 to 34.6 Pa s, at an angular frequency of $\omega = 10\,\mathrm{rad\,s^{-1}}$. Differential scanning calorimetry (DSC) showed glass transition temperature (T_g) of −43 to −55 °C. The liquid OPVs were blue emissive and had monomeric characteristics due to efficient

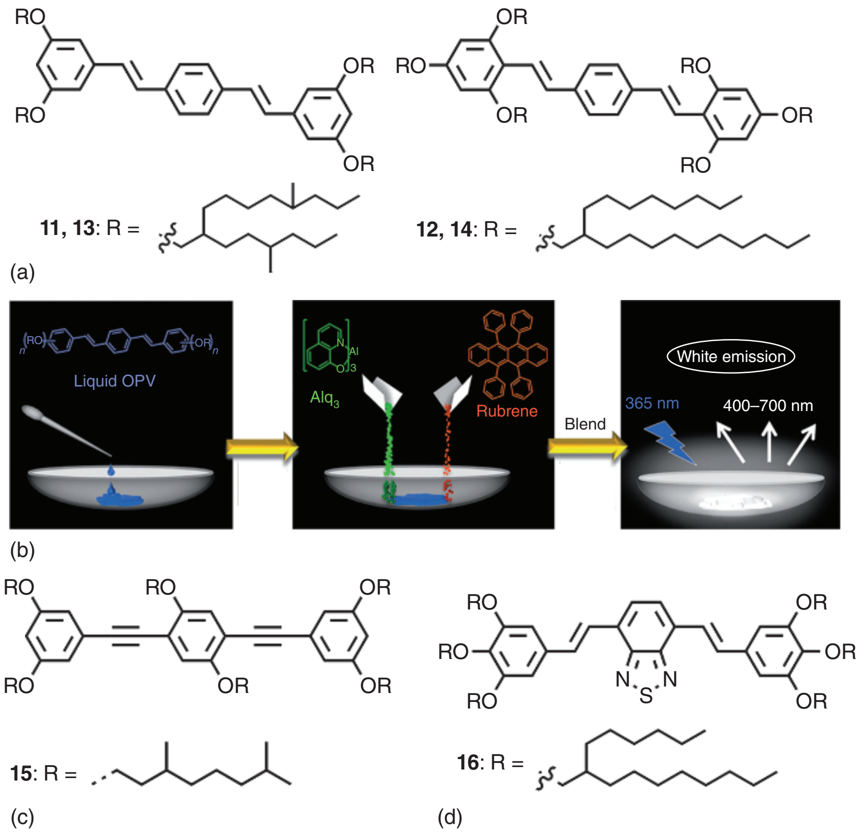


Figure 1.4 FMLs with π-conjugated oligomer unit: chemical structures of liquid (a) OPV and (b) schematic representation of using a liquid OPV as a matrix for making white-light-emitting liquid composite; chemical structures of liquid (c) OPE and (d) BTD. Source: Reproduced with permission from Babu et al. [25]. Copyright 2012, John Wiley & Sons.

isolation of the OPV unit by wrapping with the bulky branched alkyl chains. Furthermore, they were employed as a dispersion medium for various acceptor dopants, such as green-emitting tris(8-hydroxyquinolinato) aluminum (Alq_3) and orange-emitting 5,6,11,12-tetraphenylnaphthacene (rubrene) (Figure 1.4b); and the composite liquid showed white light emission with a chromaticity diagram coordinate value of (0.33, 0.34). The white-light-emitting liquid can be painted on substrates of various shapes and geometries as well as used as an ink for roller ball pens.

1.3.6.2 Oligo-(*p*-phenyleneethylene)s (OPEs)

In a follow-up work of the liquid OPVs, a liquid oligo-(*p*-phenyleneethylene)s (OPE) functionalized with multiple branched alkyl chains was reported [26]. The melting point of **15** was found to be 21 °C, proving that the compound was a liquid at above room temperature (Figure 1.4c). In this case, the substitution of multiple alkyl chains could not effectively isolate the OPE unit. This was suggested by a redshift in the absorption and fluorescence spectra of the solvent-free state compared to those in solution. The redshift in the absorbance and fluorescence spectra indicates aggregation of molecules governed by π–π interactions in the solvent-free state.

1.3.6.3 Benzothiadiazoles (BTDs)

Benzothiadiazoles (BTDs) are known as strongly electron-accepting dyes which are fluorescent in red color both in solution and in the bulk solid state. Recently, the group of Ishi-i reported BTDs containing electron-donating triphenylamines that emitted red light [27]. However, the emission was quenched in polar solvents. A recent effort from the same group was successful in appending BTD dyes with electron-rich tris(alkyloxy)phenylethene and creating BTD-based electron donors [28]. Interestingly, these produced efficient red light emission in solvents of all polarity and was also red emissive in the bulk solvent-free state. A branched alkyl chain derivative of BTD (substituted with C_2C_6 chain) was a red viscous liquid at room temperature (**16**, Figure 1.4d). By a strategy of donor–acceptor conjugation, the authors were successful in creating red-light-emitting materials with large Stokes shift. The development of red-emitting dyes is important because red is one of the three primary colors, and also for biological applications.

1.3.7 Porphyrins

Porphyrins have been widely used for various optical and electronic applications, such as in solar cells, transistors, electroluminescent materials, sensors, and nonlinear optics. Due to the strong π–π interactions among the large π-conjugated macrocyclic units, porphyrins have a strong tendency to form a self-assembled state. Many of the porphyrins have been reported to exist in solid state and to have poor solubility in organic solvents. This makes the optoelectronic applications of this class of molecules a formidable challenge. Easily processable analogs of porphyrins, such as in the LC state or in the liquid state for greater convenience, are therefore desirable. Linear alkyl-chain-substituted porphyrin derivatives were synthesized and investigated by the research groups of Maruyama [29] and Gryko [30] independently in 2010. Meso-substituted porphyrins bearing 3,4,5-trialkoxyphenyl substituents **17a**–**c** (Figure 1.5a) were obtained as liquids at room temperature and employed as dispersion media for electron acceptors such as C_{60} and carbon nanotubes (CNTs). On the other hand, investigation was carried out by Gryko and coworkers on almost the same series of porphyrins, but **17c** was described as a solid at room temperature. Furthermore, detailed investigations by this group revealed that alkyl chain lengths below C_9H_{19} and above $C_{12}H_{25}$ on these porphyrin derivatives yielded solids at room temperature. For further detailed discussions of the studies by Gryko on porphyrin derivatives, refer to Chapter 2.

1.3.8 Fullerenes

In contrast to pristine fullerene C_{60}, which is practically insoluble in any organic solvent except aromatic ones like chlorobenzene, substitution of alkyl chains

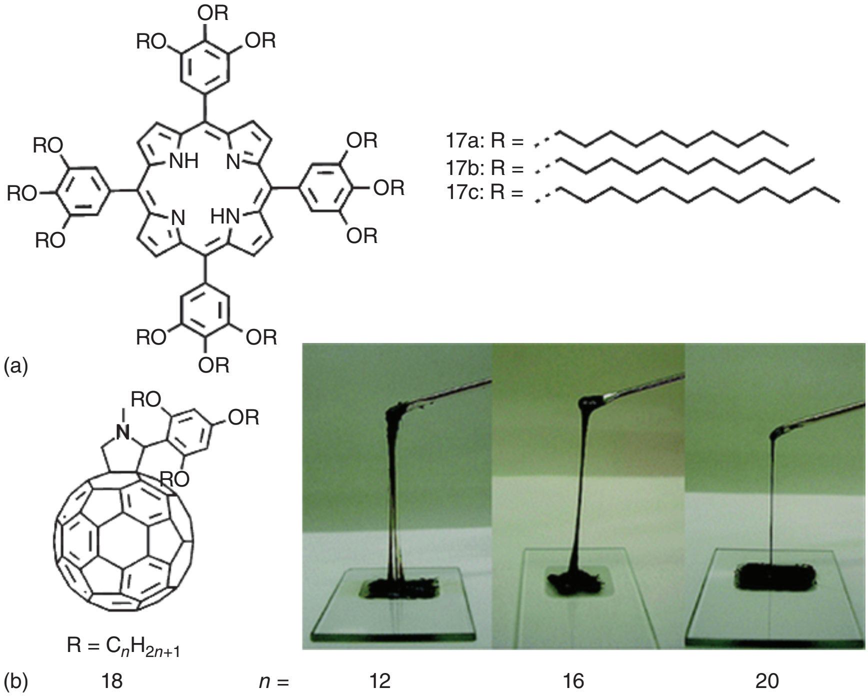


Figure 1.5 Chemical structures of series of (a) alkylated liquid porphyrins **17** and (b) liquid fullerene derivatives **18**; (c) photographs of the liquid fullerenes containing linear-alkyl chain lengths of 12, 16, and 20 (oligomethylene unit's number) respectively, showing their liquid nature. Source: Reproduced with permission from Michinobu et al. [31]. Copyright 2006, American Chemical Society.

not only increases the solubility but also tunes their phase from solid to liquid [31]. The chain length, nature of alkyl chain, and the substitution position have a great impact on the viscosity and the physical nature of the liquid fullerenes. C_{60} derivatives (18) with linear alkyl chains substituted on 2,4,6-tris(alkyloxy) phenyl group (Figure 1.5b) showed a clear decrease in the viscosity values with increasing chain lengths [31, 32]. While the derivative with $C_{12}H_{25}$ side chains had a complex viscosity value on the order 10^5 Pa s, the derivatives with $C_{16}H_{33}$ and $C_{20}H_{41}$ alkyl substitutions had viscosities on the order 10^4 and 10^3 Pa s, respectively, indicating a more fluid-like behavior (Figure 1.5b). Moreover, the derivative with shorter alkyl chains, C_8H_{14} was a solid, indicating stronger π–π interactions among C_{60} units. More details on liquid fullerenes, including branched alkyl-chain-substituted C_{60} and C_{70} derivatives and their studies on directed assembly using a concept of "hydrophobic amphiphile" can be found in Chapter 9.

1.4 Alkylsilane-Chain-Appended π-Molecular Liquids

Another strategy to create FMLs is by substituting alkylsilane chains on the π-conjugated dye unit. The commonly used moieties are polysiloxane chains, and their oligomeric counterparts. The siloxane chains effectively introduce amorphicity into the materials. Another advantage of this substitution could probably be the hydrophilicity provided by these functional groups. However, this aspect has not been explored. Although very few examples are available for this class of molecules, they deserve a mention because of their strategy and useful applications.

1.4.1 Triarylamines

Liquid triarylamines **19**, **20** (Figure 1.6a,b) were synthesized by substituting silyl ethers onto a triarylamine unit [33]. This substitution considerably lowers the T_g and suppresses the crystallization tendency of these compounds (Figure 1.6c). Bender and coworkers carefully optimized the Piers–Rubinsztajn reaction for the synthesis of many liquid triarylamine derivatives [34]. They also performed detailed studies on the charge-transport properties of liquid triarylamines and proved that the molecular motions have negligible impact on the macroscopic charge-transport properties of a liquid semiconductor [35]. The hole mobility of liquid triarylamine **19** was found to be 1.92×10^{-3} cm^2 V^{-1} s^{-1}, well in accordance with the values reported for the nonliquid analogs.

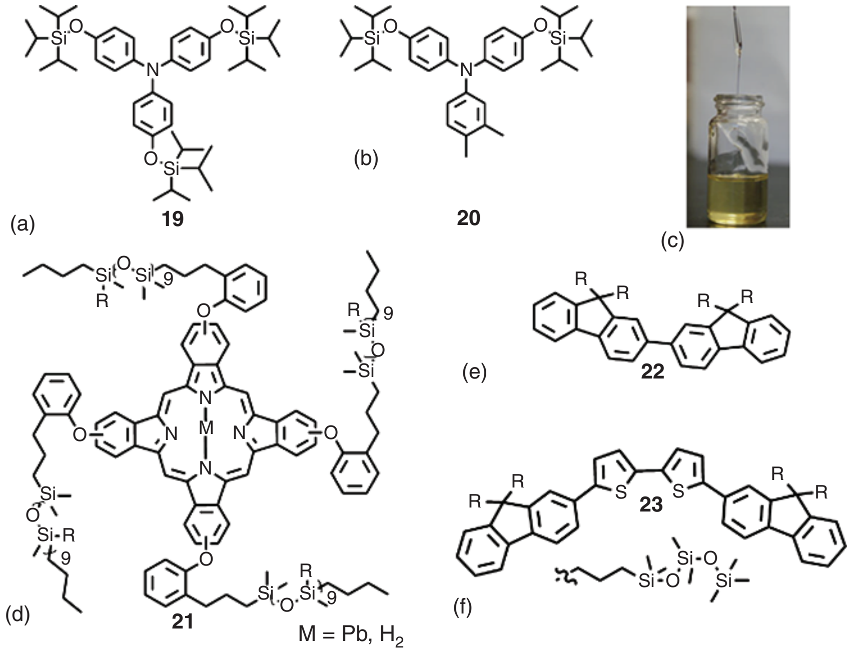


Figure 1.6 Alkylsilane-chain-appended FMLs: (a,b) triarylamines; (c) photograph of liquid triarylamine; (d) phthalocyanine; (e,f) oligofluorenes. Source: Adapted with permission from Kamino et al. [33]. Copyright 2011, American Chemical Society.

1.4.2 Phthalocyanines

A series of isotropic liquid phthalocyanines were successfully synthesized by appending poly(dimethylsiloxane) chains onto a phthalocyanine unit. The research on liquid phthalocyanines carried out by Maya et al. was aimed at thermorefractive properties of a silicone fluid and nonlinear optical properties of phthalocyanine chromophore [36]. Phthalocyanines are known to possess a large reverse saturable optical absorption by virtue of their larger absorption cross-section in the excited state compared to their ground state. The metal-free and Pb-substituted derivatives were synthesized and studied (**21**, Figure 1.6d). Those liquids were viscous, with the metal-free derivative having a T_g of 14 °C and the Pb-substituted derivative having a T_g of 3 °C.

The concept was extended to more polysiloxane derivatives [37]. The refractive index could be varied with temperature. A large negative thermorefractive coefficient was obtained, which was similar in magnitude to that observed from neat siloxanes. Detailed analysis through nonlinear transmission, transient absorption, z-scan, and degenerate four-wave mixing studies was performed. The studies proved that the liquid phthalocyanines substituted with Pb have a broad spectral region of induced absorption.

Linear or branched alkyl-chain-substituted liquid phthalocyanines have been also developed very recently in our group [38, 39], and showed complex rheology phenomena and redox-coupled spin switching as well as visible color tuning. Macrocyclic oligopyrroles, i.e. porphyrins and phthalocyanines, can form a metal complex and also its axial ligand coordinations; thus, these liquid substances could have many other possibilities in applications.

1.4.3 Oligofluorenes

Adachi and coworkers successfully synthesized room-temperature oligofluorene liquids [40]. The design strategy was based on functionalization of the fluorene core with alkylsiloxane side chains (Figure 1.6e,f). The fluidity conferred by the siloxane chains is effective in disrupting the π-stacking interactions of the fluorene units. Oligofluorenes are well known to have superior charge-transport and lasing properties. These properties make this chromophore a multifunctional moiety for application in optoelectronics. A major problem so far had been the defect-free fabrication of these materials in devices, which was made possible by this approach. The alkyl siloxane chains do not interfere with the properties of the π-functional core. The charge-transport properties of **22** and **23** were investigated by the TOF technique. A nondispersive ambipolar charge transport was observed. The hole and electron mobility of **22** were found to be around 7.5×10^{-5} and 1.5×10^{-5} cm^2 V^{-1} s^{-1}, respectively. **23** had a hole and electron mobility of 1×10^{-4} and 1.2×10^{-4} cm^2 V^{-1} s^{-1}, respectively, which are 1 order of magnitude higher than those of **22**. The charge-transport properties of **23** were found to improve upon increasing the electric field, in contrast to **22**. Furthermore, the lasing properties were investigated. Very low amplified stimulated emission (ASE) thresholds of 1.4 and 22 μJ cm^{-2} were obtained for both liquid oligofluorenes, respectively.

1.5 Analytical Tools for Functional Molecular Liquids

The most striking feature of FMLs is their liquid physical properties. The fluidity and amorphous features distinguish them from crystalline solids and ordered self-assembled phases. These properties limit the analytical tools available for characterization and investigation of this class of molecules. This section discusses the most commonly used techniques along with unconventional probes used to gain deep insights into the structure and properties of neat liquid substances.

1.5.1 Analytical Tools for Bulk Physical Properties

1.5.1.1 Structural Analysis

The order and disorder in FMLs is one of the highly disputed topics. Fluid matter is known to be generally disordered, but localized ordered domains may be present in alkylated π-molecular liquids, due to the interaction of the π-conjugated cores. Conventional wide-angle X-ray diffraction techniques are not suitable, as the central core units are separated in nanometer length scale regimes by attached bulky side chains. In this regard, small- and wide-angle X-ray scattering (SWAXS) in capillary mode is a better technique. The small-angle profiles obtained give a picture of the average distance of the π-conjugated units and the wide-angle profiles provide average alkyl chain distance as a common halo signal. In relatively ordered LC-like samples, SWAXS analysis would result in assignable peaks, resulting in well-defined molecular packing, like hexagonal and lamellar. SANS has also been used as a useful tool as neutrons scatter from the nuclei. Due to the multiple alkyl (hydrocarbon) chains, a good contrast is obtained by the scattering of neutrons by hydrogen and deuterium, when the sample is prepared with deuterated alkane solvents.

1.5.1.2 Microscopy Techniques

Optical microscopy (OM) in the bright field mode and polarized optical microscopy (POM) mode have been commonly employed for the characterization of FMLs. These techniques probe the microscale ordering/homogeneous isotropic nature of the liquid sample. Neat liquid samples sandwiched between cover slides are observed directly under the microscope with/without temperature control.

1.5.1.3 Rheology

Rheology is one of the highly informative tools with respect to the chemistry of fluids. Rheology measurements give us an estimate of the storage modulus (G') and the loss modulus (G''); for liquids, the G'' should be greater than the G'. It thus gives a quantitative definition to liquids. More importantly, rheology analysis gives us the complex viscosity of the liquid sample, which is a very important parameter in correlating the other physical properties observed. The angular frequency vs. strain curve helps us categorize whether the liquid has Newtonian or non-Newtonian behavior. Newtonian liquids exhibit a constant complex viscosity under frequency sweep with strain.

1.5.1.4 Calorimetric Techniques

Calorimetric analysis is very important in defining the phase transitions occurring in a liquid. While the decomposition temperature of the FMLs can be determined by thermogravimetric analysis (TGA), DSC can give very valuable information regarding the phases. It is commonly observed that liquids have a very low T_g. Special phenomena such as supercooling effect were observed in the case of a few FMLs (see details in Chapter 6) [21, 41]. In a few cases, external parameters like ramp rate, hold time at a particular temperature, and quenching at a desired temperature give us useful information regarding the liquid physical nature of the samples.

1.5.2 Analytical Tools for Spectroscopic Properties

Conventional spectroscopic tools used for the characterization of solutions, in general, can be applied to the same characterization of FMLs. However, a few modifications in the instrumental setup are sometimes necessary to make it suitable for FMLs. These details are discussed here.

1.5.2.1 UV–vis Analysis

The UV–vis instrument can be used for measuring the absorption of the samples. However, the neat sample should be sandwiched between glass/quartz plates, or coated onto one side of the plate as thin as possible and measured. The absorption spectra obtained in the neat state are broader than in the solution state, if there are intermolecular interactions. Completely disordered and chromophoric core isolated samples result in an almost identical absorption spectral feature as the monomeric species. In some neat liquids, the absorption spectra need to be recorded in the integrated sphere set up in the reflectance mode for better resolution.

1.5.2.2 Fluorescence Measurements

The fluorescence spectra can be easily recorded by sandwiching the neat sample between glass/quartz plates and by using the front-face geometry for recording the spectra. Another way is to place the sandwiched slide onto one face of a special prismatic cuvette and carry out the fluorescence measurements in normal geometry.

1.5.2.3 Fluorescence Lifetime Analysis

The fluorescence lifetime of neat samples can be recorded with a similar sample configuration as for the UV–vis and fluorescence measurements. Interesting phenomena such as phosphorescence and excimer formation have been confirmed by these measurements.

1.5.2.4 FTIR Measurements

The Fourier transform infrared (FTIR) of solvent-free, neat liquids can be carried out in the attenuated total reflectance (ATR) or kbr method.

1.6 Conclusion

The rational design of FMLs has increased new opportunities to create novel ultimately soft materials for applications that have never been explored before. The systematic softening of π-conjugated molecules from insoluble solids to liquid crystals to amorphous, neat liquids at room temperature proves a clever design of molecular architectonics. This field is a relatively new area, where the molecular design is simple, but handling liquid substances, characterizing them in depth and channelizing them to proper application are formidable challenges. Although many techniques have been explored for the characterization, the subtle balance of order and disorder in these amorphous paradigms poses a challenge for the detailed analysis of FMLs. A lot more needs to be done, and, thereby, this novel research field of FMLs opens the door to many unexplored regimes which may prove useful to all kinds of soft and fluidic materials in future.

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