Electronic supplementary information

Photo-induced guest-host interactions produce chiral conglomerates in a smectic phase

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1. Characterization of trimers **I-7**, **I-8**, **I-9** and **I-10**.

2. **Table S1.** Phase transition temperatures of mixtures containing trimer **I-*n*** (20 wt%) and compound **II** (80 wt%) on a glass slide with a cover glass with 365 nm UV irradiation at a power of 20 mW cm^{-2}. The cooling rate was 5 °C min^{-1}.

3. **Fig. S1** (a) Optical texture of trimer **I-8** in the N phase at $T–T_{Iso–N}$ = –0.5 K and (b) that under 365 nm UV irradiation at 10 mW cm^{-2}. The sample was confined in a 5 μm homogeneously aligned cell. These textures were observed between crossed polarizers.

4. **Fig. S2** (a) Optical texture of trimer **I-8** in the Cry phase at $T–T_{N–Cry}$ = –0.5 K and (b) that under 365 nm UV irradiation at 20 mW cm^{-2}. The sample was confined in a 5 μm homogeneously aligned cell. These textures were observed between crossed polarizers.

5. **Fig. S3** (a) Optical texture of a mixture of trimer **I-11** (20 wt%) and compound **II** (80 wt%) in the coexistence of the N and X phases at 81.2 °C, (b) that of the mixture with 365nm UV irradiation at 20 mW cm^{-2} at 81.2 °C, (c) that of the mixture at 4 minutes after turning off the UV light. The sample was confined in a 5 μm homogeneously aligned cell. These textures were observed between crossed polarizers.

6. **Fig. S4** (a) Optical texture of a mixture of trimer **I-11** (20 wt%) and compound **II** (80 wt%) in the coexistence of the SmC and X phases at 74.8 °C, (b) that of the mixture

with 365nm UV irradiation at 20 mW cm^{-2} and (c) that of the mixture at 4 minutes after turning off the UV light. The sample was confined in a 5 μm homogeneously aligned cell. The textures were observed between crossed polarizers. White bars indicate 500 μm.

7. **Fig. S5** Optical textures of the photo-induced phase of trimer **I-11** (20 wt%) and compound **II** (80 wt%) at 48.2 °C. The sample confined in a 5 μm homogeneously aligned cell was cooled from the isotropic liquid with 365 nm UV irradiation at a power of 20 mW cm^{-2}. R indicates the rubbing direction.

8. **Fig. S6** Optical texture of a mixture of trimer **I-11** (20 wt%) and compound **II** (80 wt%) cooling from the isotropic liquid with 365 UV irradiation at a power of 20 mW cm^{-2} between crossed polarizers at 51.4 °C. The sample was on a glass plate with a cover glass. The crystalline phase can be seen in the upper left of the texture.

9. **Fig. S7** Optical textures of a mixture of trimer **I-11** (20 wt%) and compound **II** (80 wt%) in the Cry at 33.5°C between crossed polarizers.

10. **Fig. S8** Optical textures of a mixture of trimer **I-7** (20 wt%) and compound **II** (80 wt%) in the SmC phase cooling from the isotropic liquid with 365 UV irradiation at a power of 20 mW cm^{-2} between crossed and decrossed polarizers at 74.5 °C. The sample was on a glass plate with a cover glass.

11. **Fig. S9** Optical textures of a mixture of trimer **I-8** (20 wt%) and compound **II** (80 wt%) in the SmC phase cooling from the isotropic liquid with 365 UV irradiation at a power of 20 mW cm^{-2} between crossed and decrossed polarizers at 64.4 °C. The sample was on a glass plate with a cover glass.

12. **Fig. S10** MOPAC models for *cis*-isomers of trimers **I-8** and **I-9**.

Characterization of trimers **I-7**, **I-8**, **I-9** and **I-10**.

4, 4'-Bis{11-[4-(5-hexylpyrimidin-2-yl)phenyloxy]heptyloxy}azobenzene (I-7)

^{1}HNMR (500 MHz, $CDCl_3$, TMS) : δ＝8.56 (s, 4H, Ar-**H**), 8.34 (d, 4H, Ar-**H**, *J*=8.5 Hz), 7.85 (d, 4H, Ar-**H**, *J*=9.1 Hz), 6.98 (d, 8H, Ar-**H**, *J*=8.0 Hz), 4.04 (t, 8H, -O-C**H**$_2$-, *J*=6.6 Hz), 2.59 (t, 4H, Ar-C**H**$_2$, *J*=7.7 Hz), 1.84 (quint, 8H, aliphatic-**H**, *J*=6.9 Hz), 1.64 (quint, 4H, aliphatic-**H**, *J*=7.4 Hz), 1.55-1.30 (m, 24H, aliphatic-**H**), 0.89 (t, 6H, -C**H**$_3$, *J*=6.9 Hz)

IR (KBr):ν cm^{-1}:2937, 2853 (C-Hstr), 1603,1581,1428 (C=Cstr,C=Nstr), 1252 (C-Ostr)

Elemental analysis (%): Calc. for $C_{58}H_{74}N_6O_4$: C, 75.78; H, 8.11; N, 9.14. Found C, 76.20; H, 8.22; N, 9.36.

4, 4'-Bis{11-[4-(5-hexylpyrimidin-2-yl)phenyloxy]octyloxy}azobenzene (I-8)

^{1}HNMR (500 MHz, $CDCl_3$, TMS) : δ＝8.56 (s, 4H, Ar-**H**), 8.33 (d, 4H, Ar-**H**, *J*=8.6 Hz), 7.85 (d, 4H, Ar-**H**, *J*=9.1 Hz), 6.98 (d, 8H, Ar-**H**, *J*=8.0 Hz), 4.03 (t, 8H, -O-C**H**$_2$-, *J*=6.6 Hz), 2.59 (t, 4H, Ar-C**H**$_2$, *J*=7.4 Hz), 1.82 (quint, 8H, aliphatic-**H**, *J*=7.0 Hz), 1.63 (quint, 4H, aliphatic-**H**, *J*=7.4 Hz), 1.50-1.28 (m, 28H, aliphatic-**H**), 0.89 (t, 6H, -C**H**$_3$, *J*=6.9 Hz)

IR (KBr):ν cm^{-1}:2938, 2852 (C-Hstr), 1605,1580,1429 (C=Cstr,C=Nstr), 1245 (C-Ostr)

Elemental analysis (%): Calc. for $C_{60}H_{78}N_6O_4$: C, 76.07; H, 8.30; N, 8.87. Found C, 76.23; H, 8.18; N, 8.93.

4, 4'-Bis{11-[4-(5-hexylpyrimidin-2-yl)phenyloxy]nonyloxy}azobenzene (I-9)

^{1}HNMR (500 MHz, $CDCl_3$, TMS) : δ＝8.56 (s, 4H, Ar-**H**), 8.33 (d, 4H, Ar-**H**, *J*=9.1 Hz), 7.85 (d, 4H, Ar-**H**, *J*=9.1 Hz), 6.97 (d, 8H, Ar-**H**, *J*=9.2 Hz), 4.03 (t, 8H, -O-C**H**$_2$-, *J*=6.6 Hz), 2.59 (t, 4H, Ar-C**H**$_2$, *J*=7.4 Hz), 1.82 (quint, 8H, aliphatic-**H**, *J*=7.0 Hz), 1.63 (quint, 4H, aliphatic-**H**, *J*=7.4 Hz), 1.48-1.29 (m, 32H, aliphatic-**H**), 0.89 (t, 6H, -C**H**$_3$, *J*=6.9 Hz)

IR (KBr):ν cm^{-1}:2937, 2850 (C-Hstr), 1603,1582,1429 (C=Cstr,C=Nstr), 1250 (C-Ostr)

Elemental analysis (%): Calc. for $C_{62}H_{82}N_6O_4$: C, 76.35; H, 8.47; N, 8.62. Found C, 76.90; H, 8.68; N, 8.81.

4, 4'-Bis{11-[4-(5-hexylpyrimidin-2-yl)phenyloxy]decyloxy}azobenzene (I-10)

^{1}HNMR (500 MHz, $CDCl_3$, TMS) : δ＝8.56 (s, 4H, Ar-**H**), 8.33 (d, 4H, Ar-**H**, *J*=8.6 Hz), 7.85 (d, 4H, Ar-**H**, *J*=9.1 Hz), 6.98 (d, 8H, Ar-**H**, *J*=8.6 Hz), 4.02 (t, 8H, -O-C**H**$_2$-, *J*=6.3 Hz), 2.59 (t, 4H, Ar-C**H**$_2$, *J*=7.7 Hz), 1.81 (quint, 8H, aliphatic-**H**, *J*=6.9 Hz), 1.64 (quint, 4H, aliphatic-**H**, *J*=7.3 Hz), 1.48-1.31 (m, 38H, aliphatic-**H**), 0.89 (t, 6H, -C**H**$_3$, *J*=6.9 Hz)

IR (KBr):ν cm^{-1}:2920, 2850 (C-Hstr), 1604,1582,1430 (C=Cstr,C=Nstr), 1245 (C-Ostr)

Elemental analysis (%): Calc. for $C_{64}H_{86}N_6O_4$: C, 76.61; H, 8.64; N, 8.38. Found C, 76.56; H, 8.36; N, 8.39.

Table S1. Phase transition temperatures of mixtures containing trimer **I-*n*** (20 wt%) and compound **II** (80 wt%) on a glass slide with a cover glass with 365 nm UV irradiation at a power of 20 mW cm^{-2}. The cooling rate was 5 °C min^{-1}.

Trimer	Phase transition temperatures (°C)
I-7	Iso 165.1 N 87.9 N + SmC 66.7 SmC 44.1 Cry
I-8	Iso 174.0 N 76.2 N + SmC 68.5 SmC 43.1 Cry
I-9	Iso 164.8 N 66.2 N + SmC 55.2 SmC + Cry 45.6 Cry
I-10	Iso 166.8 N 80.0 N + SmC 72.2 SmC 42.7 Cry
I-11	Iso 162.8 N 77.9 N + SmC 55.1 SmC + Cry 42.2 Cry

(a) (b)

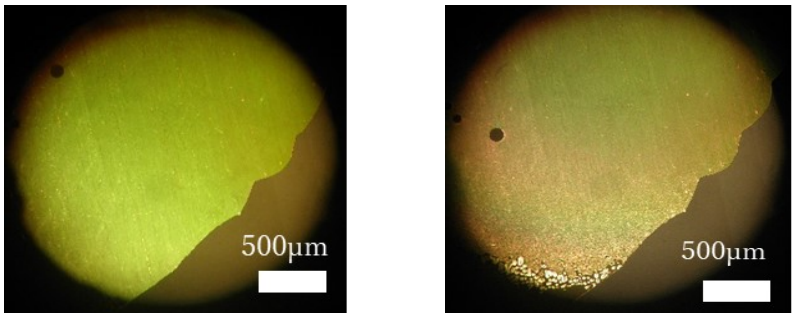


Fig. S1 (a) Optical texture of trimer **I-8** in the N phase at $T–T_{Iso–N}$ = –0.5 K and (b) that under 365 nm UV irradiation at 10 mW cm^{-2}. The sample was confined in a 5 µm homogeneously aligned cell. These textures were observed between crossed polarizers.

(a) (b)

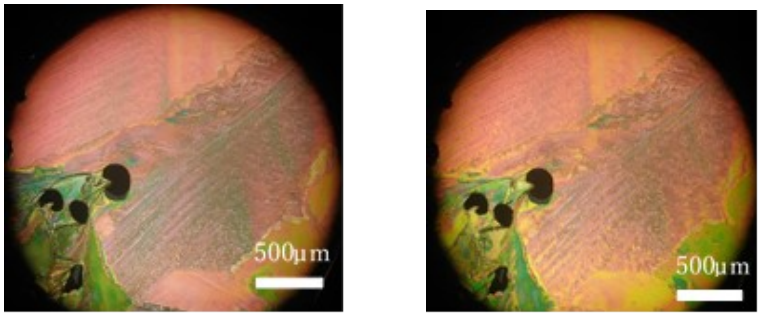


Fig. S2 (a) Optical texture of trimer **I-8** in the Cry phase at $T–T_{N–Cry} = –0.5$ K and (b) that under 365 nm UV irradiation at 20 mW cm^{-2}. The sample was confined in a 5 μm homogeneously aligned cell. These textures were observed between crossed polarizers.

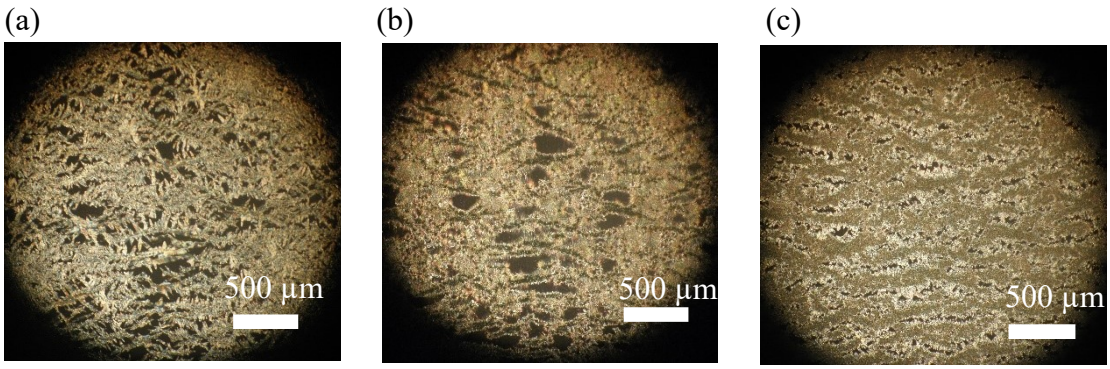


Fig. S3 (a) Optical texture of a mixture of trimer **I-11** (20 wt%) and compound **II** (80 wt%) in the coexistence of the N and X phases at 81.2 °C, (b) that of the mixture with 365nm UV irradiation at 20 mW cm^{-2} at 81.2 °C, (c) that of the mixture at 4 minutes after turning off the UV light. The sample was confined in a 5 µm homogeneously aligned cell. These textures were observed between crossed polarizers.

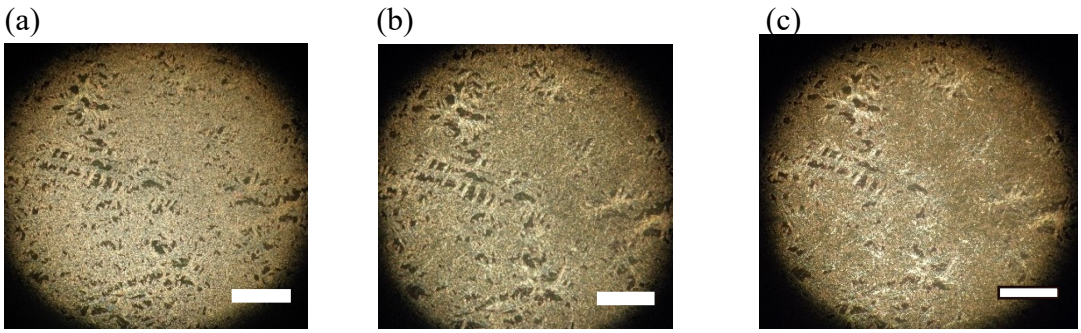


Fig. S4 (a) Optical texture of a mixture of trimer **I-11** (20 wt%) and compound **II** (80 wt%) in the coexistence of the SmC and X phases at 74.8 °C, (b) that of the mixture with 365nm UV irradiation at 20 mW cm^{-2} and (c) that of the mixture at 4 minutes after turning off the UV light. The sample was confined in a 5 μm homogeneously aligned cell. These textures were observed between crossed polarizers. White bars indicate 500 μm.

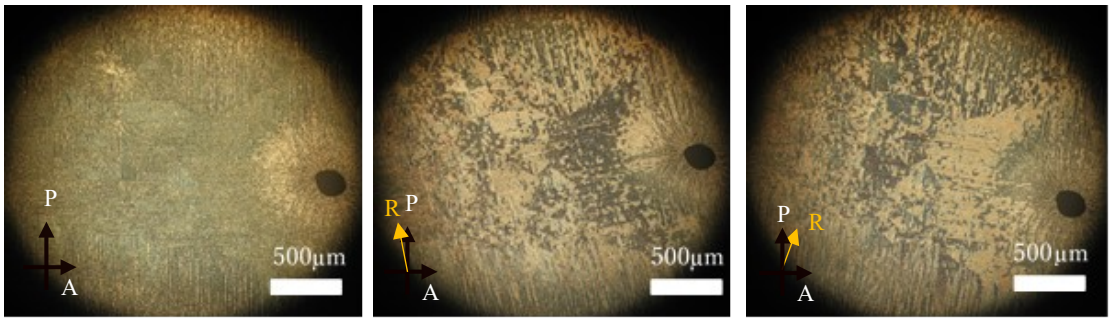


Fig. S5 Optical textures of the photo-induced phase of trimer **I-11** (20 wt%) and compound **II** (80 wt%) at 48.2 °C. The sample confined in a 5 μm homogeneously aligned cell was cooled from the isotropic liquid with 365 nm UV irradiation at a power of 20 mW cm^{-2}. R indicates the rubbing direction.

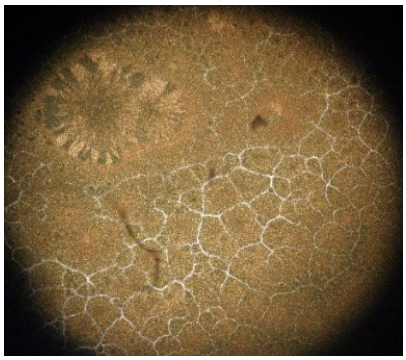


Fig. S6 Optical texture of a mixture of trimer **I-11** (20 wt%) and compound **II** (80 wt%) cooling from the isotropic liquid with 365 UV irradiation at a power of 20 mW cm^{-2} between crossed polarizers at 51.4 °C. The sample was on a glass plate with a cover glass. The crystalline phase can be seen in the upper left of the texture.

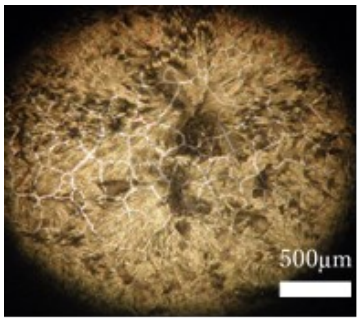


Fig. S7 Optical textures of a mixture of trimer **I-11** (20 wt%) and compound **II** (80 wt%) in the Cry at 33.5°C between crossed polarizers.

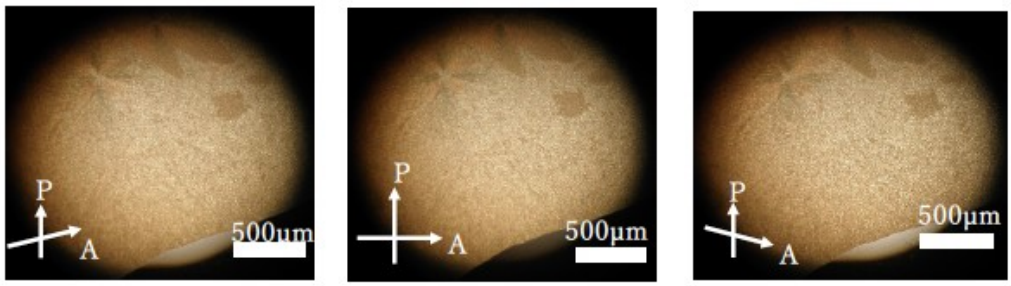


Fig. S8 Optical textures of a mixture of trimer **I-7** (20 wt%) and compound **II** (80 wt%) in the SmC phase cooling from the isotropic liquid with 365 UV irradiation at a power of 20 mW cm^{-2} between crossed and decrossed polarizers at 74.5 °C. The sample was on a glass plate with a cover glass.

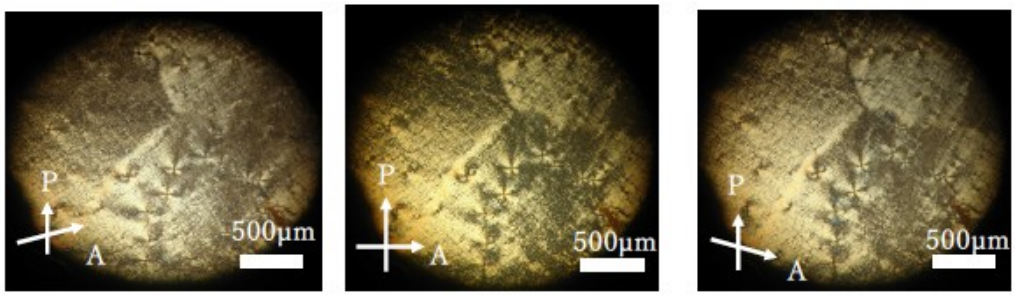
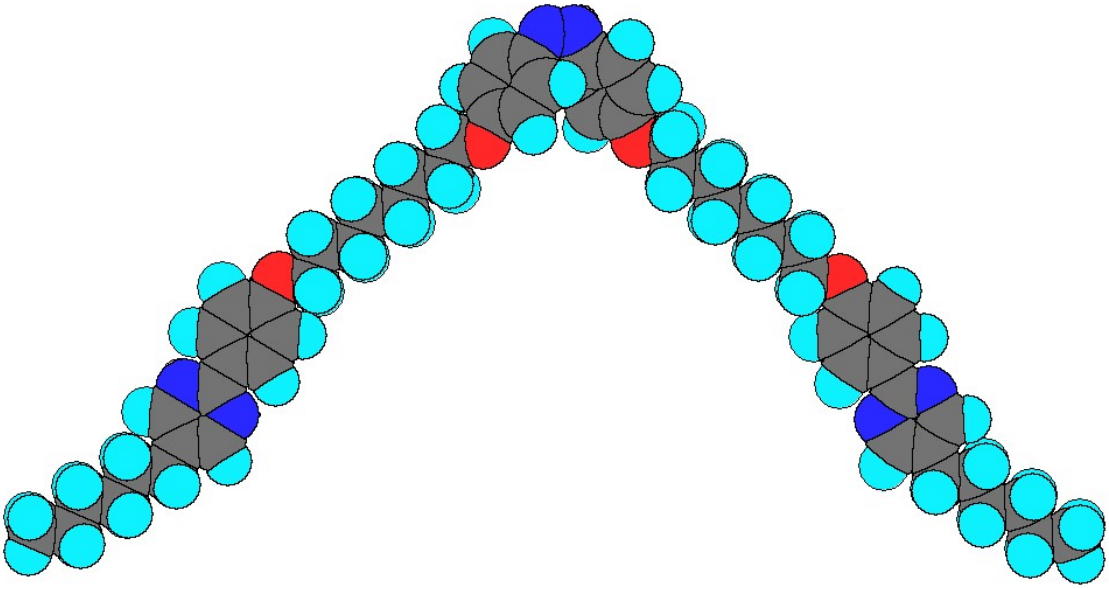


Fig. S9 Optical textures of a mixture of trimer **I-8** (20 wt%) and compound **II** (80 wt%) in the SmC phase cooling from the isotropic liquid with 365 UV irradiation at a power of 20 mW cm^{-2} between crossed and decrossed polarizers at 64.4 °C. The sample was on a glass plate with a cover glass.

(a) **I-8**



(b) **I-9**

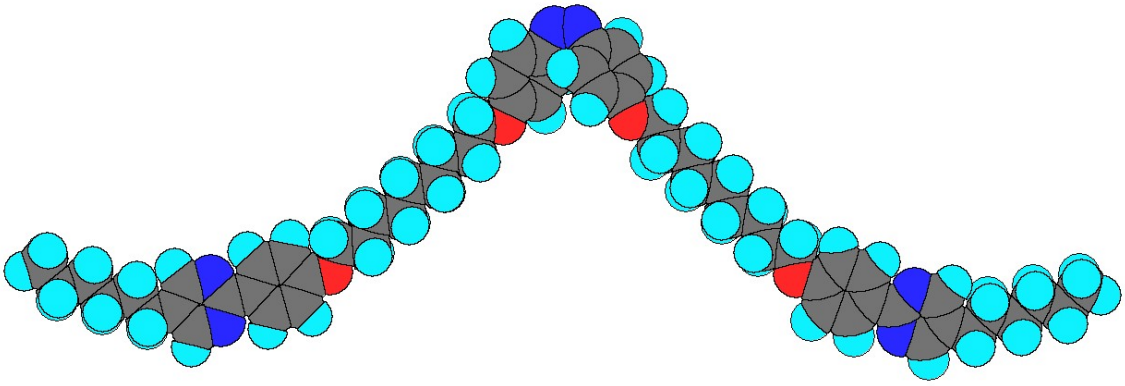


Fig. S10 MOPAC models for *cis*-isomers of trimers **I-8** and **I-9**.